PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES

INDIA

1963

Vol. XXXIII SECTION - A Part IV

Collisional Processes

Proceedings of a Symposium
held during the
Thirty-First Annual Session
at Dehradun
February 10 to12, 1962

FOREWORD

This volume contains papers presented in the Symposium of Collisional Processes sponsored by the National Academy of Sciences, India. The meeting took place during the Thirty-first Annual Session of the Academy and was held at Dehra Dun from 10 to 12 March, 1962.

It may be recalled that two big conferences were held on collisional problems in recent years—the first one in New York in 1958 and the second one in Boulder in 1961. The conference held at Dehra Dun may be considered as the third of its kind. Because of the rapid development of the subject, another conference is contemplated to be held in London during the summer of 1963.

The symposium was divided into four sessions, the first one was devoted to Elastic Collisions, the second and the third to Inelastic Collisions. In the last session, Collisional Processes in Geophysical and Chemical problems were considered.

It is my pleasure to acknowledge our indebtedness to those who gave their time and energy to the successful conclusion of the symposium, in particular to the foreign scientists who participated in the symposium.

Department of Applied Physics
University of Allahabad
Allahabad

S. N. GHOSH
Chairman

CONTENTS

Page

Foreword ... 485

Elastic Collisions

1. Elastic Scattering of Fast Protons by Spheroidal Nuclear Potential with Diffuse Boundary, by *D. Basu, S. K. Dutta and N. C. Sil* 491

2. Elastic Scattering of 1 Mev Neutrons by Complex Nuclei, by *M. Z. R. Khan and M. Shafi* ... 496

3. Pais Approximate Formula for the Phase Shift and Electron Scattering in the Thomas-Fermi Theory, by *T. Tietz* ... 500

Inelastic Collisions

4. An Analytical Formula for the Scattering Amplitudes of the Electron Detachment for the Negative Hydrogen Ion by Electron Impact, by *T. Tietz* ... 507

5. The Rotational Excitation of Molecular Nitrogen by Slow Electrons, by *A. Dalgarno and R. J. Moffett* ... 511

6. Production of NO^+ in a Mass Spectrometer Containing Nitrogen and Oxygen, by *J. F. Paulson and R. L. Mosher* ... 522

7. Total Ionization and Charge Transfer Measurements in the Energy Range 100 - 500 KeV, by *J. B. Hasted* ... 530

8. A Simplification of the Second Born Approximation, by *B. L. Moiseiwitsch* ... 537

9. Recent Work on Problems of Electron Collisions with Atoms and Ions, by *M. J. Seaton* ... 543

10. On the Connection between the Theories of Collisions and of Atomic Spectra, by *U. Fano and F. Prats* ... 553

11. Inelastic Collision of Ions in Gases, by *S. B. Karmohapatro* ... 563

12. Excitation of Hydrogen Atom in Fast Encounter with Negative Hydrogen Ion, by *B. K. Guha* ... 573

13. Cross Section for Dissociative Recombination of Nitric Oxide, by *J. J. Gibtons and B. E. Squires, Jr.* ... 579

14. Inelastic Collisions between Atomic Systems, by *D. R. Bates* ... 611

CONTENTS

Page

15. Theory of Secondary Electron Emission from Metal Surface by High Energy Ion and Atom Bombardments, by *S. P. Khare and S. N. Ghosh* ... 617

16. Sputtering Yields by Silver and Angular Distribution of the Atoms Sputtered by Ions of Noble Gases, by *S. B., Karmohapatro and A. V. Narasinham* ... 629

17. Collisional Processes in Planetary Atmospheres, by *S. N. Ghosh and A. Sharma* ... 635

Collisional Processes in Geophysical and Chemical Problems

18. Energy Loss and Scattering of Radiation Belt Electrons in the Earth's Magnetosphere, by *A. M. Lenchek and S. F. Singer* ... 701

19. Free Energy Consideration in two Electron Transfer Reactions between Two Ions in Solutions, by *B. Krishna and B. P. Sinha* 717

20. Szilard—Chalmers' Reaction in Elementary Iodine, by *H. J. Arnikar and D. K. Sharma* ... 720

21. Chemical Interaction between Hydrocarbons and Picric Acid in the Solid State, by *R. P. Rastogi, Parmjit S. Bassi and S. L. Chadha* 724

22. Collision Processes Involving Phonon & Magnon, by *K. P. Sinha and U. N. Upadhyaya* ... 732

ELASTIC COLLISIONS

ELASTIC SCATTERING OF FAST PROTONS BY SPHEROIDAL NUCLEAR POTENTIAL WITH DIFFUSE BOUNDARY

By

D. BASU, S. K. DUTTA *and* N. C. SIL

Department of Theoretical Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32

ABSTRACT

Here we have investigated the effect of introducing a diffusivity of Woods-Saxon type at the boundary of a nuclear potential of prolate spheroidal shape. The cross section of elastic scattering of 96 Mev protons by tantalum nucleus has been calculated by the Born approximation method, the theoretical result is in good agreement with experiment.

INTRODUCTION

The nuclear shell model predicts that the heavy nuclei which are far removed from the closed shell structure possess an appreciable spheroidal deformation. The presence of the electrical quadrupole moment of the nucleus and the experimentally observed energy levels of rotational spectra have been explained by assuming a spheroidal deformation of the nucleus. The sign of the quadrupole moment determines the nature of the deformation which in most cases are found to be of prolate spheroidal type. It is natural to conclude that these deformations of shape will influence the potential field generated by such a nucleus. We propose to investigate such an influence on the elastic scattering of fast protons by a semitransparent prolate spheroidal nucleus. It is hoped that a comparison of the theoretical and experimental results of scattering will indicate the explicit shape of the nucleus.

In a previous paper by Dutta and Sil (1962) the cross section of elastic scattering of 96 Mev protons by prolate spheroidal nucleus has been calculated with a constant depth and sharp cut-off semitransparent nuclear potential. The calculation has indicated that such a potential is adequate to explain the correct positions of the maxima and minima in the differential cross section curve but is inadequate in predicting very large values of differential cross-section at large angles in comparison with the experimental findings. In order to remedy the above inadequacy we propose to choose the Woods-Saxon potential which is modified suitably to account for the spheroidal shape and differs from the previous one in having a diffuse boundary instead of sharp cut-off. The Woods-Saxon potential in spherical form has been extensively applied in many nuclear processes with satisfactory results. It is natural to expect that the same potential in sphroidal form will give better agreement with experimental results. The coulomb field is due to the uniform distribution of protons within the nucleus. Here we have neglected the spin-orbit coupling term which will form the subject matter of a subsequent paper. We have calculated by Born approximation the differential cross section of elastic scattering of 96 Mev protons by the tentalum nucleus which possesses a large quadrupole moment and hence an appreciable spheroidal deformation. The semi-major and minor axes a and b of the nucleus are determined from the electric quadrupole moment and the volume of the deformed nuclus which has been taken equal to that of a conventional sphere with the same mass. We have taken the value of the parameters of the nuclear potential and

the radius of the nucleus from the paper of Saxon (1960). We further assume that during collision the rotation of the target nucleus due to transfer of angular momentum from the incident particle is small enough to justify its neglect in the calculation.

2. MATHEMATICAL FORMULATION

We propose to write the nuclear potential in elliptic coordinates as

$$V = \frac{-(V_1 + iV_2)}{1 + e^{(\xi - \xi_0)/a'}}$$

V_1 and V_2 are the same as that of Woods-Saxon and a' is equal to the diffusivity parameter divided by c, $\xi = \xi_0$ gives the surface of the nucleus as a prolate spheroid of rotation round the Z-axis, the semi-axes are (vide Magnus and Oberhettinger) $a = c\xi_0$ and $b = c\sqrt{\xi_0^2 - 1}$, c being half the distance between the foci of the prolate spheroid.

The coulomb potential is given by

$$U(r) = \int_{\text{Spheroid}} \frac{\rho_1 \, d^3r'}{|r - r'|}$$

ρ_1/e being the charge density due to the uniform distribution of the portons.

The scattering amplitude by the Born's approximation method is as follows:

$$f = \frac{1}{4\pi} \cdot \frac{2\mu}{\hbar^2} \int_{\text{Spheroid}} \left\{ U(r) + V(r) \right\} e^{k.r} \, d^3r$$

$$= f_1 + f_2$$

where f_1 and f_2 are the scattering amplitudes due respectively to $U(r)$ and $V(r)$ and $K = K_i - K_f$

$$K^2 = \frac{8\mu E}{\hbar^2} \sin^2 \theta/2$$

μ being the reduced mass and E the energy of the incident proton. For the convenience of calculation it is assumed that the axis of symmetry of the prolate Spheroid is the Z-axis and that the vector K lies in the XZ-plane. Let α be the angle of orientation, the angle between the vector K and the Z-axis.

In the previous paper, (Dutta and Sil, 1962), it is shown that the amplitude of scattering due to the coulomb potential, when the nucleus is oriented at an angle α with respect to the vector K, is given by

$$f_1 = \frac{2\mu \rho_1}{\hbar^2 K^2} \cdot \frac{(2\pi)^{3/2} b^2 a}{(a^2 K^2 \cos^2 \alpha + b^2 K^2 \sin^2 \alpha)^{3/4}} J_{3/2} \left(\sqrt{a^2 K^2 \cos^2 \alpha + b^2 K^2 \sin^2 \alpha} \right)$$

The amplitude of scattering due to the nuclear potential may be written in elliptic coordinates as

$$f_2 = \frac{-\mu}{2\pi\hbar^2}\int_1^{\infty}\int_{-1}^{+1}\int_0^{2\pi} \exp\left\{ iKc\left[\xi\eta\cos\alpha + \sqrt{(1-\eta^2)(\xi^2-1)}\cos\theta\sin\alpha\right]\right\}$$

$$\times \frac{V_1+iV_2}{1+e^{(\xi-\xi_0)/a'}}\cdot c^3(\xi^2-\eta^2)\,d\xi\,d\eta\,d\theta$$

Now making use of the relation (Watson[4], pp-20)

$$J_n(z) = \frac{1}{2\pi}\int_{\alpha}^{2\pi+\alpha} \exp\left\{ i(n\theta - z\sin\theta)\right\} d\theta$$

and putting

$$\eta = \cos\psi,\ N = \frac{\mu c^3}{\hbar^2}(V_1+iV_2)$$

$$Kc\sqrt{\xi^2-1}\sin\alpha = z\sin\beta,\ Kc\,\xi\cos\alpha = z\cos\beta$$

we get

$$f_2 = -N\int_1^{\infty}\int_0^{\pi} \exp(iz\cos\beta\cos\psi)\,J_0(z\sin\beta\sin\psi)\frac{(\xi^2-\cos^2\psi)}{1+e^{(\xi-\xi_0)/a'}}\sin\psi\,d\xi\,d\psi$$

With the help of the following relation (Watson, pp-379),

$$\int_0^{\pi} \exp(iz\cos\theta\cos\psi)\,J_{\nu-\frac{1}{2}}(z\sin\theta\sin\psi)\,C_r^{\nu}(\cos\theta)\,\sin^{\nu+\frac{1}{2}}\theta\,.\,d\theta$$

$$= (2\pi/z)^{\frac{1}{2}}\,i^r\,\sin^{\nu-\frac{1}{2}}\psi.\ C_r^{\nu}(\cos\psi)\,J_{\nu+r}(z)$$

we obtain

$$f_2 = -\int_1^{\infty}\frac{d\xi}{1+e^{(\xi-\xi_0)/a'}}\cdot\left[N\left(\frac{2\pi}{Kc}\right)^{\frac{1}{2}}\cdot\left(\frac{1}{\sqrt{\xi^2-\sin^2\alpha}}\right)^{\frac{1}{2}}\left\{ (\xi^2-1/3)\,J_{\frac{1}{2}}(Kc\sqrt{\xi^2-\sin^2\alpha})\right.\right.$$

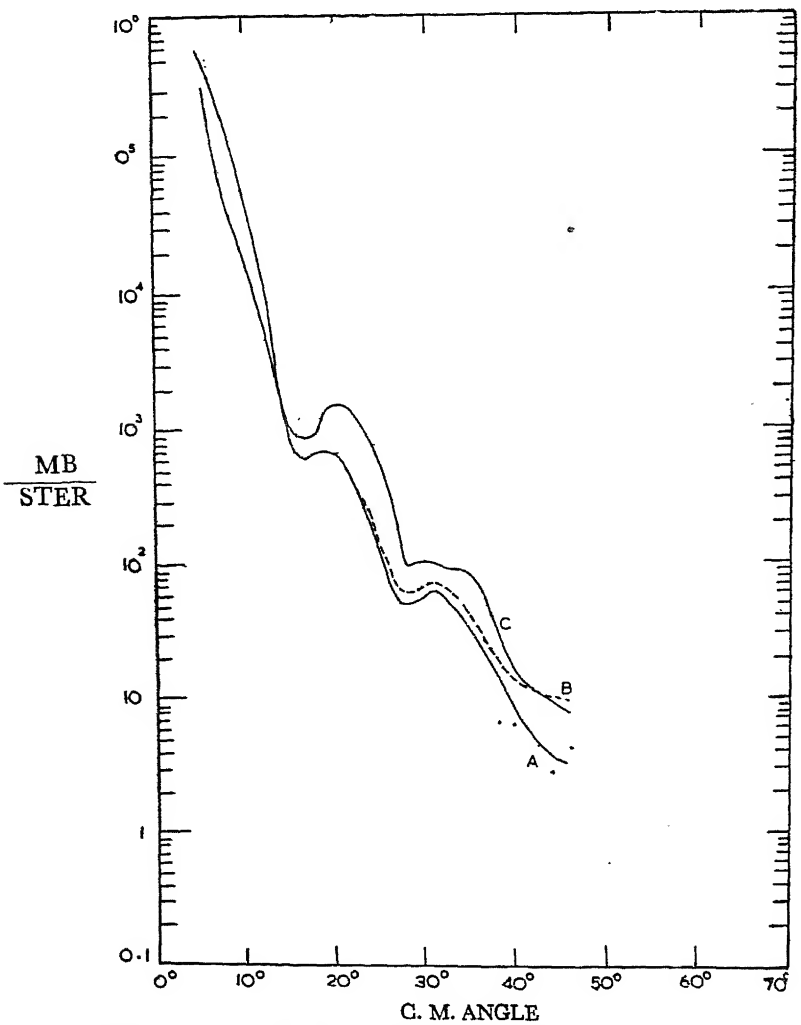
$$\left.\left. +\tfrac{1}{8}\left(\frac{2\xi^2-\sin^2\alpha(3\xi^2-1)}{\xi^2-\sin^2\alpha}\right)\times J_{5/2}\left(Kc\sqrt{\xi^2-\sin^2\alpha}\right)\right\}\right].$$

Integrating by parts, we get

$$f_2 = \frac{(-1)\sqrt{2\pi}.N}{a}\cdot\int_1^{\infty}\frac{e^{(\xi-\xi_0)/a'}}{\left[1+e^{(\xi-\xi_0)/a'}\right]^2}\,\xi(\xi^2-1)\,\frac{J_{3/2}(Kc\sqrt{\xi^2-\sin^2\alpha})}{(Kc\sqrt{\xi^2-\sin^2\alpha})^{3/2}}d\xi$$

$$= \frac{(-2)\,N}{K^2 c^2 a} \int_1^\infty \frac{\sin(Kc\sqrt{\xi^2-\sin^2\alpha})}{Kc\sqrt{\xi^2-\sin^2\alpha}} \cdot \frac{d}{d\xi} \left[\frac{(\xi^2-1)\; e^{(\xi-\xi_0)/a'}}{\left\{1+e^{(\xi-\xi_0)/a'}\right\}^2} \right] d\xi.$$

This is the scattering amplitude due to the nuclear potential when the nucleus is oriented at an angle α and the integral is numerically evaluated. The differential cross section for the nucleus oriented at an angle α is obtained by taking the modulus square of the sum of the scattering amplitudes due to the nuclear and coulomb potentials. The averaging over all orientations of the nucleus is carried out by integrating numerically the differential cross section with respect to cos α from 0 to 1.



Tantalum elastic scattering differential cross section. *A* is the extrapolated experimental elastic cross section obtained by subtracting the lowlying inelastic events from the upper limit of elastic scattering which is curve *B* and *C* is the theoretical curve.

The theoretical values of the elastic scattering cross section of 96 Mev protons by tantalum nucleus are compared with the experimental findings of Gerstein, Niederer and Strauch (1957).

We have used the values of the parameters given by Saxon (1960).

$$R = r_0 A^{1/3} \quad , \; r_0 = 1{\cdot}25 \text{ fermi}$$

$$V_1 = 45 \text{ Mev}, \; V_2 = 20 \text{ Mev}. \; E = 96 \text{ Mev}.$$

the value of the diffusivity parameter for spherically symmetric potential is 0·65, from which we have $a' = 0{\cdot}1434$.

3. RESULTS AND DISCUSSION

In the previous calculation of scattering of protons by tantalum nucleus, it has been shown that the differential cross section obtained when a spheroidal deformation is introduced in a rectangular potential shows less pronounced minima than that of rectangular well. However, beyond the scattering angle of 10°, the theoretical values of the spheroidal model are considerably large compared with experimental findings. When we introduce the diffusivity of the boundary of the spheroidal well, the value of the scattering cross section comes down and follows quite closely the pattern of the experimental curve. The experimental data are available upto 45° angle and the comparison is limited upto that angle.

Because the potential depends also on the angle variables, the conservation of the angular momentum is ensured only by transfer of angular momentum from the incident particle to the target nucleus, this transfer sets the latter into slow precessional motion. However, the precession is so slow that one is justified in considering the nucleus as stationary for the scattering process as pointed out by Margolis[6].

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ELASTIC SCATTERING OF 1 MEV NEUTRONS BY COMPLEX NUCLEI

By

M. Z. R. KHAN *and* M. SHAFI

Department of Physics, Muslim University, Aligarh

ABSTRACT

The angular distributions of 1 Mev neutrons elastically scattered from complex nuclei have been calculated using the diffuse optical model. The previous calculations of Feschbach *et al*[1] using the square well model did not reproduce the secondary maximum near 90° as was found experimentally by Walt and Barschall[2] for the nuclei around mass number 200. The present calculations are found to be in better agreement with the experimental data.

INTRODUCTION

When total neutron cross sections are measured at low energies with good resolution instruments, sharp peaks and troughs are observed. When the cross sections are averaged over may individual resonances the so called "gross structure" problem is obtained which can be explained by a complex potential.[1]

The complex potential model has been very successful in reproducing total cross sections and fairly successful in explaining the scattering cross sections and the angular distributions of elastic scattering for very wide range of nucleon energies. At low energy the comparison of elastic scattering with theoretical calculations is complicated by the presence of compound elastic scattering in the experimental measurements. According to the model the compound elastic scattering is a part of 'absorption'.

DIFFERENTIAL CROSS SECTION FOR ELASTIC SCATTERING

The square well optical model has been used by several authors (e. g. ref. (1)). This is able to explain some of the essential features of the experimental data. However the 1 Mev data of Walt and Barsschall[2] for the differential cross section of elastic scattering show apart from the forward peaking a secondary maximum near 90° in case of nuclei around mass number 200. In their calculations Feschbach *et. al*[1] using the square well model obtained the angular distributions of shape elastic scattering, but the secondary maximum was not reproduced. The discrepency between the experimentally observed and the computed distributions remained even after adding a plausible estimate of the angular distribution of the compound elastic scattering to the shape elastic distribution.

A number of authors have shown that the sharp boundary of the sqaure well potential is responsible for many draw backs (e. g. Ref. 3, 4). In this work the following potential has been employed for the calculation of the angular distribution of shape elastic scattering of 1 Mev neutrons.

$$V(r) = -(V_0 + i W_0) - \frac{V_{s,0}}{1{\cdot}4r} \exp\left(\frac{r-R}{a_{s.0}}\right)^2 \vec{\sigma}.\vec{l} \qquad 0 \leqslant r \leqslant b$$

$$= -V_0 \exp\left(\frac{r-b}{a_{s.g}}\right)^2 - i W_0 - \frac{V_{s.0}}{1{\cdot}4r} \exp\left(\frac{r-R}{a_{s.0}}\right)^2 \vec{\sigma}.\vec{l} \qquad b < r \leqslant (R+2)$$

$$= -V_0 \exp\left(\frac{r-b}{a_{s.g}}\right)^2 - \frac{V_{s.o}}{1{\cdot}4r} \exp\left(\frac{r-R}{a_{s.o}}\right)^2 \vec{\sigma} \cdot \vec{l}\, r > (R+2)$$

where

$$R = r_0 A^{1/3} \; ; r_0 = 1{\cdot}22$$

$$a_{s.g} = 2{\cdot}32 \; ; a_{s.o} = 1{\cdot}2$$

$$V_0 = 47$$

$$b = R - 1{\cdot}93$$

all lengths being in fermis and all energies in Mev.

Exact calculations have been done to compute the distributions shown in Figures 1 (a), 1 (b) and 1 (c). The parameters used for computing the distribution

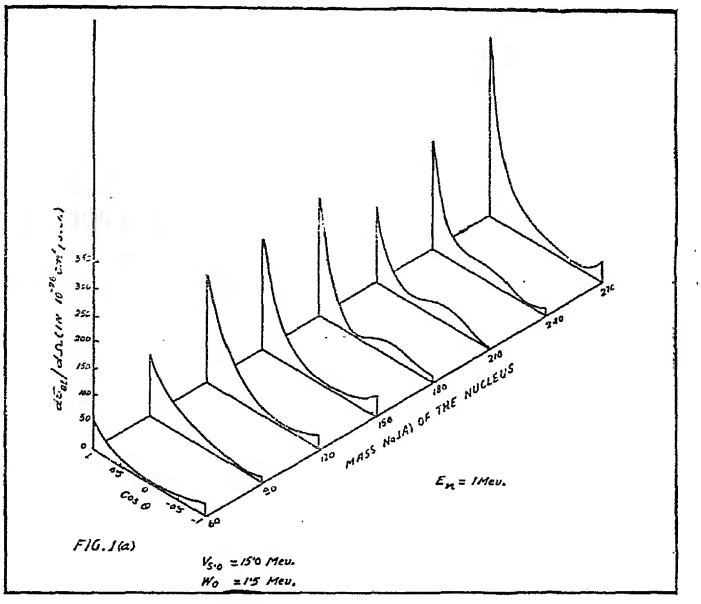


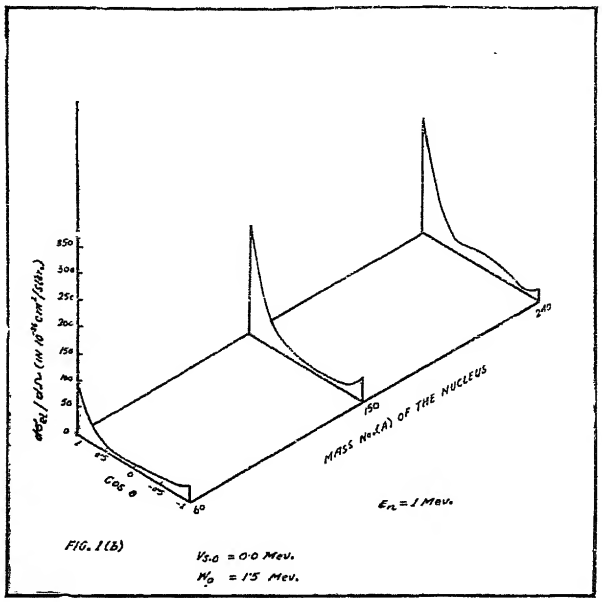
FIG. 1(a)

shown in fig. 1 (a) are those that fit the low energy cross section and polarization data.

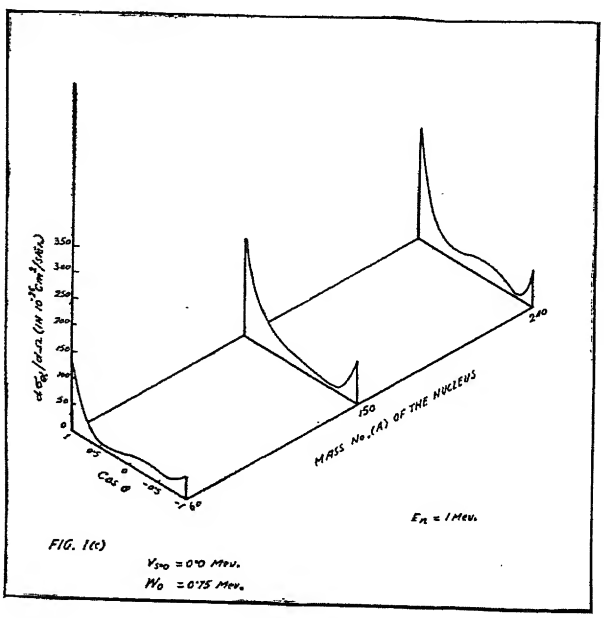
DISCUSSION

The angular distributions plotted in fig. 1 (a) show that the secondary maximum near 90° around mass number 200 is clearly reproduced by the theoretical curves. Inclusion of the compound elastic scattering will almost certainly not change the shape of the angular distribution, because among the experimental measurements[2] in the region around mass number 200 there are nuclei like Bi, Pb, Hg, etc. which have negligible deformation of the core and high spins. As shown in ref.

(1) the compound elastic scattering will have a spherically symmetric distribution for such nuclei. Thus for such nuclei when the present computed distributions are corrected for the compound elastic scattering the shape of the distribution



will not change and their agreement with the experimental data would still remain. The nuclei with low spins like W, Th, etc. have highly deformed cores,



and so the data for these nuclei should be compared with the theoretical calculations which take into account the deformation of the nuclei.

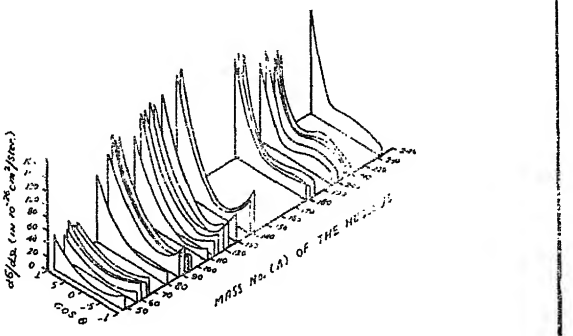


FIG. 2. DIFFERENTIAL CROSS SECTION FOR ELASTIC SCATTERING OF 1-MeV NEUTRONS. [Ref (2)]

The cross sections near $\theta = 180^0$ will be sufficiently increased to agree with the experimental values when the compound elastic scattering is added. However near $\theta = 0$ the calculated cross sections are slightly higher than the experimentally observed values. This defect will clearly be enhanced by the inclusion of compound elastic scattering. This discrepency is however also present in the work of ref. (1). Figs 1 (a), 1 (b) and 1 (c) show how strongly the shape of the distribution depends on the choice of the optical model parameters. Quite possibly the discrepency for the forward angle scattering may also be removed by a slight variation of some of the parameters and then a good general agreement between the experimental and the theoretical distributions obtained.

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4. R. D. Woods and D. S. Saxon, *Phys. Rev.* **95**, No. 2, 1954.

Added in the Proof : Recently it has been established (M. Z. R. Khan, *Nuclear Physics*, **41** 629, 1963) that the imaginary potential is peaked in the surface region at low energies. It is quite likely that a calculation with a surface peaked distribution may improve the situation.

PAIS APPROXIMATE FORMULA FOR THE PHASE SHIFT AND ELECTRON SCATTERING IN THE THOMAS-FERMI THEORY

By

T. TIETZ

Department of Theoretical Physics, University of Łódź, Łódź (Poland)

ABSTRACT

In this paper we calculate the phase shift of electron scattering with atoms by means of a simplified Pais method. The calculation of this paper shows that this simplified Pais method for the phase shift gives better results than the Born approximation and nearly the same results as the accurate Pais method. Our method has this advantage that it is more practical than the Pais method.

The collision of electron with atoms is as known a many-body problem. As such it is necessary to apply an approximate method for finding the phase shift appearing in the scattering amplitude $f(\vartheta)$ given by the Faxen and Holtzmark[1].

$$f(\vartheta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1).(e^{2i\delta_l} - 1) P_l(\cos\vartheta) \tag{1}$$

This formula for the scattering of electrons with atoms is valid for a central field. δ_l appearing in eq. (1) is the phase shift. In case if the quantum number l is large enough we can apply for estimating δ_l the Born approximation, but for low quantum numbers l, the Born approximation is unsuitable for determining δ_l, since in this case we obtain for the phase shift δ_l the results of small accuracy. When the Born approximation is no longer useful we can apply the Pais method[2] for finding the phase shift. The Pais principle can be formulated in the following way. We write the radial wave equation in the form

$$\frac{d^2w_l}{dr^2} + \left[k^2 - \frac{l(l+1) - c^2}{r^2} \right] w_l = 0 \tag{2}$$

where c is the constant. Since the solution w_l must satisfy the following boundary conditions

$$w_l(0) = 0 \text{ and } w_l(\infty) \to \sin\left(kr - \frac{l\pi}{2} + \delta_l \right) \tag{3}$$

then the constant c fulfilles the relation

$$(l+1/2) - 2\delta_l / \pi = \sqrt{(l+1/2)^2 - c^2} \tag{4}$$

and the solution w_l of eq. (2) which fulfills the boundary conditions (3) has the form

$$w_l(r) = \sqrt{\frac{\pi kr}{2}}\, J_{l+1/2} - (2\delta_l/\pi)^{(kr)} \tag{5}$$

Using the Pais variational method or the method preposed by the author[3] one obtains for δ_l the following formula

$$\frac{2l+1-(2\delta_l/\pi)}{2l+1-(4\delta_l/\pi)}\,\delta_l = -\frac{m\pi}{\hbar^2}\int_0^\infty r\,V(r)\;J^2_{l+1/2\,-(2\delta_l/\pi)}(kr)\,dr \tag{6}$$

where $V(r)$ is a central field. Formula (6) obtained for the first time by Pais has this disadvantage that for the phase shift δ_l we obtain a transcendental equation, as well as this method is unsuited for the determination of zero order phase shift. In order to simplify the Pais method of eq. (6) for practical calculations we can expand $f(\vartheta)$ eq. (1) as follows

$$f(\vartheta)=(1/k)\sum_{l=0}^{\infty}(2l+1)\;[\delta_l - 2/3\;\delta_l{}^3+\ldots+i\,(\delta_l{}^2-1/3\;\delta_l+\ldots)\,]\,P_l\,(\cos\vartheta) \tag{7}$$

The usual first Born approximation for $f(\vartheta)$ we obtain dropping of in eq. (7) all terms except δ_l and replacing δ_l by the first approximation.

$$\delta_l{}^{(1)} = -\frac{\pi m}{\hbar^2}\int_0^\infty V(r)\,J^2_{l+\frac{1}{2}}(kr)\,r\,dr \tag{8}$$

The symbol J in eqs. (5), (6) and (8) denotes the Bessel function characterising the free particle solution. If we develop δ_l as a series in powers of the interaction potential $V(r)$ namely

$$\delta_l = \delta_l{}^{(1)} + \delta_l{}^{(2)} + \ldots \tag{9}$$

where $\delta_l{}^{(1)}$ is given by eq. (8) and δ_l is small and given by eq. (6) then we obtain for $\delta_l{}^2$ the formulas

$$\delta_l{}^{(2)}=(2/\pi)\left(a_l-\frac{\delta_l^{(1)}}{2l+1}\right)\delta_l{}^{(1)} \text{ where } a_l = -\left(\frac{\partial\delta_p}{\partial p}\right)^{(1)}_{p=l+\frac{1}{2}} \tag{10}$$

The first Born approximation for the phase shift appearing in the last equation is given by formula (8). Using formulas (8), (9) and (10) we shall calculate the phase shift δ_l for the Thomas-Fermi[4] as also analytical fits for Hartree potential given by Byatt[5]. The interaction potential based on the Thomas-Fermi and on the Hartree scheme may be written as follows.

$$V(r) = (-Ze^2/r)\;(Z_p/Z) \tag{11}$$

The Coulomb potential of the nucleus is modified by the factor Z_p/Z representing the screening effect of the orbital electrons on the nucleus. The function Z_p/Z satisfies the conditions $Z_p/Z\to 1$ as $r\to 0$ $Z_p/Z\to 0$ as $r\to\infty$. The potential will then be a Wetzel type. Ruark[6] first proposed the representation of the Hartree potentials for Z_p/Z the following form.

$$Z_p/Z = \sum_n c_n\,e^{-b_n x} \tag{12}$$

The dimensionless variable is related to r as follows

$$r = x/\mu \text{ and } \mu = 0{\cdot}88534 a_0/Z^{1/3} \qquad (13)$$

where Z is the atomic number and a_0 is the first Bohr radius of hydrogen atom. In Table I we have the numerical values of the constants c_n and b_n for the Hartree analytical fits of Z_p/Z as also for the Thomas-Fermi field.

TABLE NO. 1

Numerical values of the constants c_n and b_n according to eq. (12) for exponential fits of Z_p/Z and the Thomas Fermi function $\Phi(x)$

Element	Z_p/Z (one term)		Z_p/Z (series of terms)					
	c_1	b_1	c_1	c_2	c_3	b_1	b_2	b_3
He	1·00	−1·60	1·25	−0·25	..	1·75	3·845	...
Be	...	...	1·00	−0·48	0·48	0·574	1·081	3·06
C	...	...	1·25	−0·44	0·19	0·828	1·41	4·29
N	1·00	0·95	1·20	−0·32	0·12	0·904	1·43	9·65
O	1·00	0·919	1·25	−0·35	0·10	0·991	1·63	18·3
F	1·00	0·907	...	...	..	...	...	...
Ne	1·00	0·978	...	...	...	...	...	...
A[a]	...	...	0·84	−0·24	0·40	0·566	1·056	3·25
A	...	...	0·659	0·341	...	0·574	2·77	—
K	...	...	0·124	0·68	0·196	0·0514	0·765	2·80
Ca	...	...	0·20	0·56	0·24	0·195	0·770	3·08
Cr	1·00	0·731	1·00	−0·20	0·20	0·731	1·26	3·70
Fe	...	...	0·25	0·56	0·19	0·335	0·828	3·76
Zn	...	...	0·22	0·78	...	0·319	1·081	...
Ge	...	...	0·22	0·78	...	0·263	1·165	...
As	...	...	0·295	0·705	...	0·387	1·295	...
Br	...	...	0·360	0·640	...	0·366	1·485	...
Kr[a]	...	...	0·335	0·60	0·065	0·290	1·33	7·00
Kr	...	...	0·415	0·51	0·075	0·378	1·48	7·00
W	...	...	0·19	0·72	0·09	0·216	0·970	15·00
Hg	...	...	0·19	0·56	0·25	0·257	0·779	3·16
$\Phi(x)$ Rozental		...	0·255	0·581	0·164	0·246	0·947	4·356
$\Phi(x)$ Motière		...	0·35	0·55	0·1	0·3	1·2	6·00

(a) These expressions contain a polarization correction. Some of the exponential fits Z_p/Z contain the exchange correction and some do not. Those of Z_p/Z which contain the exchange correction can be found in A. Y. Freeman, *Phys. Rev.*, **91**, 1410 (1953) as also D. R. Hartree Reports on Progress in Physics (The Physical Society London 1946) vol. **11**, p 113. More details concerning the Z_p/Z are to be found in the paper of W. J. Byatt, *Phys. Rev.*, **104**, 1298 (1956)

Substituting Z_p/Z of eq. (12) to eq. (11) we obtain for the interaction potential $V(r)$ the following formula.

$$V(r) = -\frac{Ze^2}{r}\sum_n c_n\, e^{\frac{-b_n r}{\mu}} \tag{13}$$

Using the integral representation for the Bessel function[7].

$$J^2_{l+\frac{1}{2}}(kr) = 2/\pi \int_0^{\pi/2} J_{2l+\frac{1}{2}}(2kr\cos\vartheta)\, d\vartheta \tag{14}$$

and

$$J_{2l+1}(2kr\cos\vartheta) = 2/\pi \int_0^{\pi/2} \sin[2kr\cos\vartheta\sin\Psi]\sin(2l+1)\Psi d\Psi \tag{15}$$

we can calculate a_l appearing in eq. (10). For a_l we obtain the formula

$$a_l = -\frac{8mZe^2}{\pi\hbar^2}\sum_n c_n \int_0^\infty e^{\frac{-b_n r}{\mu}} dr \int_0^{\pi/2}\int_0^{\pi/2} \Psi \sin[2kr\cos\vartheta\sin\Psi]\cos(2l+1)\Psi d\Psi d\vartheta \tag{16}$$

The integrals over r and ϑ can be easily carried out, so that for a_l we obtain

$$a_l = -\frac{4mZe^2}{\pi\hbar^2}\sum_n c_n \int_0^{\pi/2} \frac{\Psi\cos(2l+1)\Psi}{\sqrt{(b_n/\mu)^2+4k^2\sin^2\Psi}} \ln\frac{\sqrt{(b_n/\mu)^2+4k^2\sin^2\Psi}+2k\sin\Psi}{\sqrt{(b_n/\mu)^2+4k^2\sin^2\Psi}-2k\sin\Psi} d\Psi \tag{17}$$

The last formula for a_l we rewrite in atomic units

$$a_l = -\frac{4z}{\pi}\sum_n c_n \int_0^{\pi/2} \frac{\psi\cos(2l+1)\psi}{\sqrt{(b_n/\mu)^2+8E\sin^2\psi}} \ln\frac{\sqrt{(b_n/\mu)^2+8E\sin^2\psi}+2\sqrt{2E}\sin\psi}{\sqrt{(b_n/\mu)^2+8E\sin^2\psi}-2\sqrt{2E}\sin\psi} d\psi \tag{18}$$

where E is the energy of the incident electrons and its unit equals twice the ionization energy of the normal state of the hydrogen atom and is 27, 23 e-volts, and in atomic units is $0{\cdot}88534z^{-1/3}$. The constants b_n and c_n are to be found in table I. The integral over ψ appearing in formula (18) can be integrated only

numerically. The Born approximation $\delta_l^{(1)}$ for the potential eq. (13) accordingly to formula (8) gives us the expression in atomic units.

$$\delta_l^{(1)} = \frac{z}{\sqrt{2E}} \sum_n c_n Q_l \left(1+\tfrac{1}{2} \left(\frac{b_n}{\mu \sqrt{2E}} \right)^2 \right) \tag{19}$$

where Q_l are Legendre polynomials of the second kind. Formulas (9), (10), (18) and (19) allow us to calculate the phase shift δ_l appearing in eq. 9). In table II we have some numerical results for H_e for incident electron energies in the voltage range $16 \leqslant V \leqslant 340$.

TABLE II

A comparison of the phase shift δ_l eq. (9) and (10) with $\delta_l^{(1)}$ eq. (8) and numerical values.

Voltage	l	$\delta_l^{(1)}$ Born eq. (8)	$\delta_l = \delta_l^{(1)} + \delta_l^{(2)}$ eq. (9) and eq. (10)	Numerical values for δ_l (Mc.Dougall)
16	1	0·0536	0·0731	0·070
49	1	0·1340	0·1875	0·186
121	1	0·2276	0·2796	0·272
	2	0·0892	0·0924	0·0946
	3	0·0492	0·04917	...
340	1	0·2668	0·3389	0·308
	2	0·1364	0·1415	0·1524

Table II shows that our results for δ_l are significantly better than Born phases $\delta_l^{(1)}$ and only a little worse than the corresponding numerical values. Eq. (6) in our case can be presented analytically but the phases fulfill a transcendental epuation of infinite order. Our formula eq. (18) is much simpler for practical calculations than eq. (6). Table II shows that our results for δ_l agree quite well with the exact Mc.Dougall[8] values. At the high energies our results for $\delta_l^{(1)}$ are equivalent with the corresponding results for the Born approximation.

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INELASTIC COLLISIONS

AN ANALYTICAL FORMULA FOR THE SCATTERING AMPLITUDES OF THE ELECTRON DETACHMENT FOR THE NEGATIVE HYDROGEN ION BY ELECTRON IMPACT

By

T. TIETZ

Department of Theoretical Physics, University of Lódź, Lódź (Poland)

ABSTRACT

In this paper we derive the scattering amplitudes for the detachment of electrons by an electron impact from H^- in its ground $^1S_0$ state. This process is of general interest for the study of the properties of negative ions and how they compare with those of neutral atoms and positive ions.

The total cross-section for the detachment of an electron by electron impact in its ground $^1S_0$ state is

$$\sigma = \tfrac{1}{2} \int d\vec{\kappa} \iint \sin\theta d\theta d\phi \, (k_q/k_p) \left\{ \left| f_k^{(1)} - g_k^{(1)} \right|^2 + 3 \left| g_k^{(3)} \right|^2 \right\}. \qquad (1)$$

In this formula for σ the symbols $\vec{k}_q$ (k_q, θ, ϕ) and $\vec{r}_e$ are the incident, scattered, and ejected wave vectors respectively. According to Bates[1] *et al* the scattering amplitudes $f_k^{(1)}$, $g_k^{(1)}$ and $g_k^{(3)}$ appearing in formula (1) can be written in the Born Oppenheimer approximation as follows

$$\left\{ f_k^{(1)}, \; g_k^{(1)} \right\} = (2\pi)^{-1} \iiint d\tau_1 \, d\tau_2 \, d\tau_3 \exp\left(- i \vec{k}_q \cdot \vec{r}_1 \right) F_k^{(1)*} \left(\vec{r}_2, \vec{r}_3 \right)$$

$$\times \left(1/r_1 - 1/r_{12} - 1/r_{13} \right) \left\{ \exp \left(i \vec{k}_q . \vec{r}_1 \right) \Psi_o \left(\vec{r}_2 . \vec{r}_3 \right) \exp \left(i \vec{k}_p . \vec{r}_2 \right) \right.$$

$$\left. \Psi_o \left(\vec{r}_1 , \vec{r}_3 \right) \right\} \qquad (2)$$

for singlet-singlet transition and

$$g_k^{(3)} = (2\pi)^{-1} \iiint d\tau_1 \, d\tau_2 \, d\tau_3 \exp \left(- i \vec{k}_q . \vec{r}_1 \right) \Psi_k^{(3)*} \left(\vec{r}_2, \vec{r}_3 \right)$$

$$\times \left(1/r_1 - 1/r_{12} - 1/r_{13} \right) \exp \left(i \vec{k}_p . \vec{r}_3 \right) \Psi_o \left(\vec{r}_1 , \vec{r}_2 \right) \qquad (3)$$

In formula (2) and (3) Ψ_o is the ground state wave function while $\Psi_k^{(1)}$ and $\Psi_k^{(3)}$ are the final singlet and triplet wave function corresponding to one electron bound and the other electron free. Geltman[2] has shown that the scattering amplitudes given in formula (1) and (2) can be simplified in the following from.

$$f_k^{(1)} = - 4\pi^{-\frac{1}{2}} \Delta \left| \vec{k}_p - \vec{k}_q \right|^{-2} \frac{J(K)}{K}$$

$$- g_k^{(3)} = g_k^{(1)} = - 2\pi^{-\frac{1}{2}} \Delta \left| \vec{k}_p - \vec{\kappa} \right|^{-2} \frac{T(K)}{K} \qquad (4)$$

where

$$\vec{K} = \vec{k}_p - \vec{k}_q - \vec{\kappa} , \quad \Delta = \int d\tau \; \phi_o \, \phi_H , \text{ and } J(K) = \int_o^\infty d\tau \; \phi_o \sin K\tau \qquad (5)$$

In the last formula ϕ_o is the solution of a one-electron Schrödinger equation with a short range attractive potential containing one-bound $1s$ state at the known binding energy of 0·747 ev and ϕ_H is the ground state hydrogen function. In a

previous paper the author[3] has shown that ϕ_0 can be presented with sufficient accuracy as follows

$$\phi_0 = \frac{N_0}{2\sqrt{\pi}} \frac{e^{-k_0 r} - e^{-(k_0+a)r}}{r} \tag{6}$$

where N_0 is the radial normalization constant

$$N_0 = \frac{\sqrt{2k_0 (k_0+a)(2k_0+a)}}{a} \tag{7}$$

The constant a and k_0 appearing in formulas (6) and (7) have the following numerical values $a=2{\cdot}01407$ and $k_0=0{\cdot}23425$. Substituting for ϕ_0 and ϕ_H in formula (5) the expression (6) and the known normalized expression for ϕ_H we obtain after simple calculation an analytical expression for $J(K)/K$, namely

$$\frac{J(K)}{K} = 0{\cdot}226486 \left(\frac{1}{K^2+0{\cdot}054866} - \frac{1}{K^2+5{\cdot}05494} \right) \tag{8}$$

If we compare our numerical values for $J(K)/K$ as a function of K given in Table 1 accordingly to our formula (8) with the corresponding graph $J(K/K$ we see that our analytical expression eq. (8) agrees very well with the Geltman's[4] numerical value.

TABLE I

Some numerical results of our $J(K)/K$ eq. (8)

K	0·0	0·1	0·2	0·3	0·4	0·5
$J(K)/K$	4·08	3·45	2·34	1·52	1·013	0·702
K	0·6	0·7	0·8	0·9	1·0	
$J(K)/K$	0·504	0·375	0·276	0·224	0·168	

Formula (8) allows us to express analytically the scattering amplitudes $f_k^{(1)}$, $g_k^{(1)}$ and $g_k^{(3)}$ as also to calculate the total cross-section σ given by eq. (1). The detachment of electrons from negative ions by the impact of free electrons is a process which has not been yet directly measured by the laboratory. It is of astrophysical interest[5] to know to what extent the dissociation of H^- by electron

impact influences photospheric processes as also it is interesting of arc plasma investigation[6].

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THE ROTATIONAL EXCITATION OF MOLECULAR NITROGEN BY SLOW ELECTRONS

By

A. DALGARNO *and* R. J. MOFFETT

Department of Applied Mathematics, The Queen's University of Belfast, Belfast (N. Ireland)

ABSTRACT

A quantal calculation is carried out of the energy loss parameter which occurs in theories of radio wave interaction in the atmosphere and its accuracy is discussed. The limits of validity of the conventional formulation of radio wave interaction are briefly examined.

1. INTRODUCTION

Theories of radio wave interaction (cf. Bailey and Martyn 1934, Huxley 1952) involve a parameter G which relates the mean rate of electron energy loss $G\bar{\nu}$, $\bar{\nu}$ being the mean collision frequency, to the mean electron energy $\bar{E}$ according to

$$\overline{\frac{dE}{dt}} = G\bar{\nu}\left(\bar{E} - E_g\right) \quad , \tag{1}$$

where E_g is the mean thermal energy of the ambient gas. The major part of the electron cooling rate is due to the excitation of the rotational levels of molecular nitrogen and Huxley (1959) has analysed laboratory data semi-empirically to obtain for the rotational contribution to $G\bar{\nu}$

$$\left(G\bar{\nu}\right)_{\rm rot} = n\,\frac{1{\cdot}08\times10^{-7}}{T_g^{3/2}}\,\exp\left(-213/T_g\right), \tag{2}$$

where n is the number density of nitrogen molecules and T_g is the gas temperature. A comparison of (2) with the results of a quantal calculation should be instructive.

2. THEORY

According to the Born approximation, the scattering amplitude for the transition from the rotational state designated by quantum numbers j and mj and with eigenfunction $Y_j\,m_j\,(\hat{r}')$ to the rotational state designated by quantum numbers j' and m_j' and with eigenfunction $Y_j'\,m_j'\,(\hat{r}')$ is given by

$$A\left(jm_j; j'\,m_j' \mid \theta\right) = -\frac{1}{4\pi}\,\frac{2m}{\hbar^2}\int dr\,\exp\left(i\,K\,.\,r\right)$$

$$\times \int Y_j\,m_j\,(\hat{r}')\,Y_j'^{*}\,m_j'\,(\hat{r}')\,V\,(\hat{r}', r)\,d\hat{r}', \tag{3}$$

where θ is the scattering angle, $V(\hat{r}', r)$ is the interaction potential between the incident electron and the target molecule and K is the momentum change vector. Expanding the interaction potential $V(\hat{r}', r)$ according to

$$V(r', r) = \sum_{\lambda=0}^{\infty} v_\lambda P_\lambda(\hat{r}' \cdot \hat{r}) \tag{4}$$

$$= \sum_{\lambda=0}^{\infty} v_\lambda(r) \frac{4\pi}{2\lambda+1} \sum_{m=-\lambda}^{+\lambda} Y^*_{\lambda m}(K \cdot \hat{r}) Y_{\lambda m}(\hat{K} \cdot \hat{r}') \tag{5}$$

and $\exp(iK \cdot r)$ according to

$$\exp(iK \cdot r) = \sum_{l=0}^{\infty} i^l (2l+1) j_l(Kr) P_l(\hat{K} \cdot \hat{r}) \tag{6}$$

(3) becomes

$$A(j m_j; j' m_j', |\theta) = -\frac{2m}{\hbar^2} \sum_{\lambda=0}^{\infty} i^\lambda \int Y^*_{j' m_j'}(\hat{r}') Y_{j m_j}(\hat{r}') P_\lambda(\hat{K} \cdot \hat{r}') d\hat{r}'$$

$$\times \int_0^{\infty} r^2 v_\lambda(r) j_\lambda(Kr) dr. \tag{7}$$

The differential scattering cross section for the transition from level j to level j' is defined as

$$\sigma(j'; j | \theta) = \frac{k'}{k(2j+1)} \sum_{m_j=-j}^{+j} \sum_{m_j'=-j'}^{+j'} \left| A(j m_j; j' m_j', |\theta) \right|^2 \tag{8}$$

where k is the initial wave number and k' is the final wave number of the scattered electron.

Substituting (7) into (8),

$$\sigma(j', j | \theta) = \frac{k'}{k} \left(\frac{2m}{\hbar^2} \right)^2 \sum_{\lambda=0}^{\infty} \sum_{\lambda'=0}^{\infty} i^{(\lambda-\lambda')}$$

$$\times \int_0^{\infty} r^2 v_\lambda(r) j_\lambda(Kr) dr \int_0^{\infty} r^2 v_{\lambda'}(r) j_{\lambda'}(Kr) dr$$

$$\times \frac{1}{(2j+1)} \sum_{m_j=-j}^{+j} \sum_{m_j'=-j'}^{+j'} \frac{(2j+1)(2j'+1)}{(2\lambda+1)(2\lambda'+1)} C(jj' \lambda; 000)$$

$$\times C(jj' \lambda; m_j m_j' 0) C(jj' \lambda'; 000) C(jj' \lambda'; m_j m_j' 0) \tag{9}$$

where the C's are Clebsch-Gordon coefficients. The summations over the projection quantum numbers may be effected immediately to yield the result

$$\sigma(j';j\mid\theta) = \frac{k'}{k}\sum_{\lambda=0}^{\infty}\left\{\int_0^\infty r^2\,\frac{2m}{\hbar^2}\,v_\lambda(r)\,j_\lambda(Kr)\,dr\right\}^2 \times \frac{(2j'+1)}{(2\lambda+1)^2}\,C(jj'\lambda;000)^2 \tag{10}$$

The term of (4) of most importance for energy loss is that for which $\lambda = 2$ in which case $j' = j \pm 2$ and

$$\sigma(j+2;j\mid\theta) = \frac{3k'}{10k}\left\{\int_0^\infty r^2\,\frac{2m}{\hbar^2}\,v_2(r)\,j_2(Kr)\,dr\right\}^2 \times \frac{(j+1)\quad+2)}{(2j+1)\,(2j+3)} \tag{11}$$

$$\sigma(j-2;j\mid\theta) = \frac{3k'}{10k}\left\{\int_0^\infty r^2\,\frac{2m}{\hbar^2}\,v_2(r)\,j_2(Kr)\,dr\right\}^2 \times \frac{j(j-1)}{(2j-1)\,(2j+1)} \tag{12}$$

Gerjuoy and Stein (1955a) pointed out that the long range of the interaction between the electron and the molecular charge distribution is the origin of the large energy losses observed in the laboratory. The leading term in the long range interaction has the form

$$v_2(r) = -qe^2a_0^2/r^3 \tag{13}$$

where q is the quadrupole moment of the molecule, measured in atomic units. Using the result that

$$\int_0^\infty r^2\,j_2(Kr)\,\frac{dr}{r^3} = \frac{1}{3} \tag{14}$$

it follows that the scattering is isotropic and the total cross sections for rotationa excitation are

$$\sigma(j+2;j) = \frac{8k'}{15k}\,q^2\,\frac{(j+1)\,(j+2)}{(2j+1)\,(2j+3)}\,\pi a_0^2 \tag{15}$$

$$\sigma(j-2;j) = \frac{8k'}{15k}\,q^2\,\frac{j\,(j-1)}{(2j-1)\,(2j+1)}\,\pi a_0^2 \tag{16}$$

(Gerjuoy and Stein 1955a).

Gerjuoy and Stein (1955a) have argued that the first Born approximation is adequate for rotational excitation by slow electrons in that due to the long range of (13) excitation occurs at distances where distortion is small and they show by an approximate evaluation of the second Born amplitude that coupling to the other rotational levels is unimportant. There remains the possibility that coupling to excited electronic levels may be significant. At large distances, this coupling manifests itself in the familiar spherically symmetric polarization term

$$-\frac{1}{6}\left(\alpha_{\parallel}+2\alpha_{\perp}\right)\frac{e^2a_0^3}{r^4} \tag{17}$$

$\alpha_{\parallel}$ and $\alpha_{\perp}$ being respectively the parallel and perpendicular polarizabilities and in the less familiar polarization term

$$-\frac{1}{3}\left(\alpha_{\parallel}-\alpha_{\perp}\right)\frac{e^2a_0^3}{r^4}P_2\left(\hat{r}'\cdot\hat{r}\right) \tag{18}$$

which can induce rotational excitation.

We adopt the potential

$$\frac{2m}{\hbar^2}v_2(r) = -2\left(\frac{q}{r^3}+\frac{\alpha_{\parallel}-\alpha_{\perp}}{3r^4}\right) \tag{19}$$

Then using the result

$$\int_0^{\infty} r^2 j_2(Kr)\frac{dr}{r^4} = \frac{\pi K}{16} \tag{20}$$

and noting that

$$\sin\theta\, d\theta = K\, dK/kk' \tag{21}$$

we obtain for the rotational cross sections

$$\sigma(j+2;j) = \frac{k'}{15k}\pi a_0^2\left\{8q^2+\frac{\pi q(\alpha_{\parallel}-\alpha_{\perp})}{3}\left(\frac{3k^2+k'^2}{k}\right)+\frac{\pi^2(\alpha_{\parallel}-\alpha_{\perp})^2}{32}\left(k^2+k'^2\right)\right\}\frac{(j+1)(j+2)}{(2j+1)(2j+3)} \tag{22}$$

$$\sigma(j-2;j) = \frac{k'}{15k}\pi a_0^2\left\{8q^2+\frac{\pi q(\alpha_{\parallel}-\alpha_{\perp})}{3}\left(\frac{3k^2+k'^2}{k}\right)+\frac{\pi^2(\alpha_{\parallel}-\alpha_{\perp})^2}{32}\left(k^2+k'^2\right)\right\}\frac{j(j-1)}{(2j-1)(2j+1)} \tag{23}$$

3. CALCULATION OF CROSS SECTIONS

There is frequently confusion over the definition of the quadrupole moment q. Corresponding to (13), the quantal formula for a neutral homonuclear molecule with nuclear charges z is

$$q = \left\langle -\sum_{i=1}^{2z} r_i^2 P_2(\cos\theta_i) + z\frac{R^2}{2} \right\rangle \qquad (24)$$

where $\langle\ \rangle$ denotes an average over the molecular wave function, r_i is the position vector of the i th electron referred to the midpoint of the internuclear axis $\theta_i = 0$ as origin, R is the equilibrium internuclear separation and distance is measured in units of the Bohr radius a_0. A value of 1·11 for $|q|$ has been derived from measurements of collision broadening (cf, Gordy, Smith and Trambarulo 1953) whereas a value of − 1·87 for q has been obtained by Scherr (1955) in a theoretical evaluation of (24). Gerjuoy and Stein (1955a) adopted the value of 0·96 for $|q|$ suggested by Smith and Howard (1950).

In contrast to the uncertainty in the value of the quadrupole moment, the parallel and perpendicular polarizabilities are well-determined and in units of a_0^3 they are respectively 16·1 and 9·8 (cf. Hirschfelder, Curtiss and Bird 1954).

The influence of polorization on rotational excitation is illustrated in figure 1 which gives the cross sections for the transition from the level $j = 12$ to the level $j = 14$ both with and without polarization corresponding to $q = \pm 1{\cdot}11$. The sign of q obtained by Scherr is probably correct so that for N_2 polarization causes a reduction in the cross section.

The accuracy of the theoretical cross sections is not easy to assess but some evidence is provided by the work of Frost and Phelps (1961) who have analysed the electron swarm experiments. Frost and Phelps conclude that the experimental data are consistent with cross sections about 10% larger than those computed by Gerjuoy and Stein (1955a). The 12-14 cross section obtained by so modifying the results of Gerjuoy and Stein is included in figure 1.

If polarization is ignored, the results of Frost and Phelps suggest that the quadrupole moment of nitrogen has magnitude 1·01. A preliminary investigation that we have carried out suggests that if polarization is included and if q is negative it has magnitude 1·25.

Some further indication of the influence of polarization is provided by data on molecular hydrogen. For H_2, the quadrupole moment is positive so that, in contrast to N_2, polarization increases the cross section. This behaviour is in at least qualitative agreement with the conclusion of Frost and Phelps (1961) that for H_2 the swarm data demand cross sections about $2\frac{1}{2}$ times larger than those of Gerjuoy and Stein (1955b). However, part of the discrepancy for H_2 is due merely to the fact that Gerjuoy and Stein adopted a value of 0·393 for q whereas the correct value is 0·473†. The cross sections should therefore be increased by a factor of 1·45 and the discrepancy (which we suggest is largely due to polarization) is reduced to a factor of about 1·7.

† Gerjuoy and Stein may have confused the mean of the square of the equilibrium separation $\langle R^2 \rangle$ with the square of the mean $\langle R \rangle^2$.

4. ROTATIONAL ENERGY LOSSES

The rate of energy loss of an electron of energy E through excitation and de-excitation of the rotational levels of N_2 is given by

$$\left(\frac{dE}{dt}\right)_{\text{rot}} = v \sum_j n_j \left\{ \sigma(j+2; j) \left[\varepsilon_{j+2} - \varepsilon_j \right] - \sigma(j-2; j) \left[\varepsilon_j - \varepsilon_{j-2} \right] \right\}, \tag{25}$$

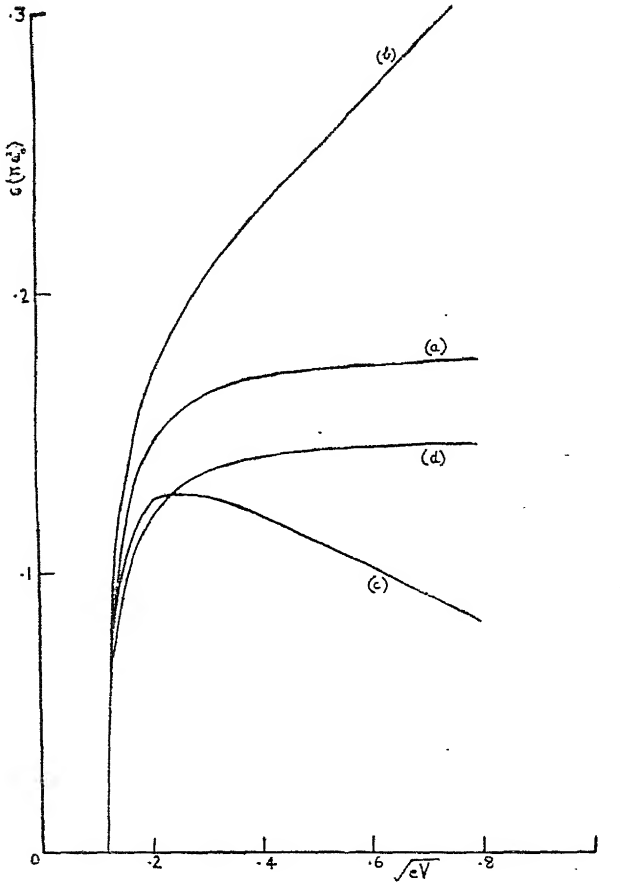

Fig. 1. Cross sections for excitation from $j = 12$ to $j = 14$ plotted against $\sqrt{(\text{incident electron energy})}$.

Curve (*a*) : without polarization, $|q| = 1{\cdot}11$
(*b*) : with polarization, $q = +1{\cdot}11$
(*c*) : with polarization, $q = -1{\cdot}11$
(*d*) : without polarization $|q| = 1{\cdot}01$

where v is the electron velocity, ε_j is the binding energy of the j th level and n_j is the number density of molecules in the j th level. If T_g is the gas temperature

$$n_j = \frac{(2j+1)\exp(-\varepsilon_j/kT_g)n}{\sum_j (2j+1)\exp(-\varepsilon_j/kT_g)} \qquad (26)$$

Experimental data are frequently expressed in terms of the mean fractional energy loss per collision which in the absence of vibrational excitation is given by

$$\lambda = \frac{2m}{M} + \frac{1}{E}\left(\frac{dE}{dt}\right)_{rot}\frac{1}{\nu}, \qquad (27)$$

where M is the mass of the molecule and the first term of λ is the loss in elastic collisions. Values of the second term of λ in units of $2m/M$ are illustrated in figure 2 for nitrogen gas at $300°K$, the adopted collision frequency ν being that measured

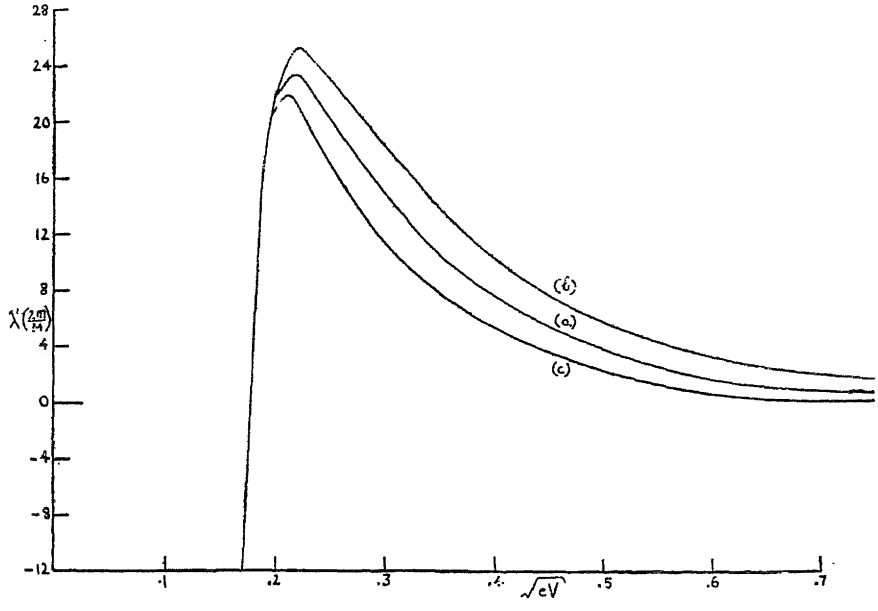

Fig. 2. Mean fractional energy loss per collision, $(\lambda)_{rot}$, plotted against $\sqrt{(\text{incident electron energy})}$, at $T_g = 300°K$
Curve (*a*) : without polarization, $|q| = 0{\cdot}96$
(*b*) : with polarization, $q = +0{\cdot}96$
(*c*) : with polarization, $q = -0{\cdot}96$

by Pack and Phelps (1961). Three curves are shown corresponding to the three curves of figure 1 (except that q was taken as $\pm$ 0·96 to facilitate comparison with the results of Gerjuoy and Stein) and it appears that λ is relatively insensitive to the inclusion of polarization in the determination of the cross sections.

5. ENERGY LOSS PARAMETER $G\bar{\nu}$

For application to the upper atmosphere, we are interested in the Maxwellian average of (25). Corresponding to an electron temperature T_e,

$$\left(\overline{\frac{dE}{dt}}\right)_{\text{rot}} = 2\pi \left(\frac{1}{\pi k T_e}\right)^{3/2} \left(\frac{2}{m}\right)^{\frac{1}{2}} \frac{n}{\sum_j (2j+1) \exp\left(-\varepsilon_j/k T_g\right)}$$

$$\times \int_0^\infty E \exp\left(-E/k T_e\right) \sum_j (2j+1) \exp\left(-\varepsilon_j/k T_g\right)$$

$$\times \left\{ \sigma(j+2; j) \left[\varepsilon_{j+2} - \varepsilon_j\right] - \sigma(j-2; j) \left[\varepsilon_j - \varepsilon_{j-2}\right] \right\} dE \quad (28)$$

When T_e is not greatly different from T_g, the straightforward evaluation of (28) leads to severe cancellation. This difficulty can be avoided by making use of the principle of detailed balancing to write (28) in the form

$$\left(\overline{\frac{dE}{dt}}\right)_{\text{rot}} = 2\pi \left(\frac{1}{\pi k T_e}\right)^{3/2} \left(\frac{2}{m}\right)^{\frac{1}{2}} \frac{n}{\sum_j (2j+1) \exp\left(-\varepsilon_j/k T_g\right)}$$

$$\times \sum_j (2j+5) \left[\varepsilon_{j+2} - \varepsilon_j\right] \exp\left(-\varepsilon_j/k T_g\right)$$

$$\times \left\{ \exp\left(-\left[\varepsilon_{j+2} - \varepsilon_j\right] / kT_e\right) - \exp\left(-\left[\varepsilon_{j+2} - \varepsilon_j\right] / k T_g\right) \right\}$$

$$\times \int_0^\infty E \sigma(j; j+2) \exp\left(-E/kT_e\right) dE \quad (29)$$

An explicity formula for $\left(G\bar{\nu}\right)_{\text{rot}}$ can be obtained from (29) by expanding it as a power series in $(T_e - T_g)$. Thus

$$\left(G\bar{\nu}\right)_{\text{rot}} = 2\pi \left(\frac{1}{\pi k T_g}\right)^{3/2} \left(\frac{2}{m}\right)^{\frac{1}{2}} \frac{n}{\sum_j (2j+1) \exp\left(-\varepsilon_j/k T_g\right)}$$

$$\times \frac{2}{3(kT_g)^2} \sum_j (2j+5) \left[\varepsilon_{j+2} - \varepsilon_j\right]^2 \exp\left(-\varepsilon_{j+2}/kT_g\right)$$

$$\times \int_0^\infty E \sigma\left(j; j+2\right) \exp\left(-E/k T_g\right) dE \quad (30)$$

We have evaluated (30) for several gas temperatures using the cross sections shown by Frost and Phelps (1961) to be consistent with swarm data and a comparison with the formula (2) of Huxley is made in figure 3. The agreement is not

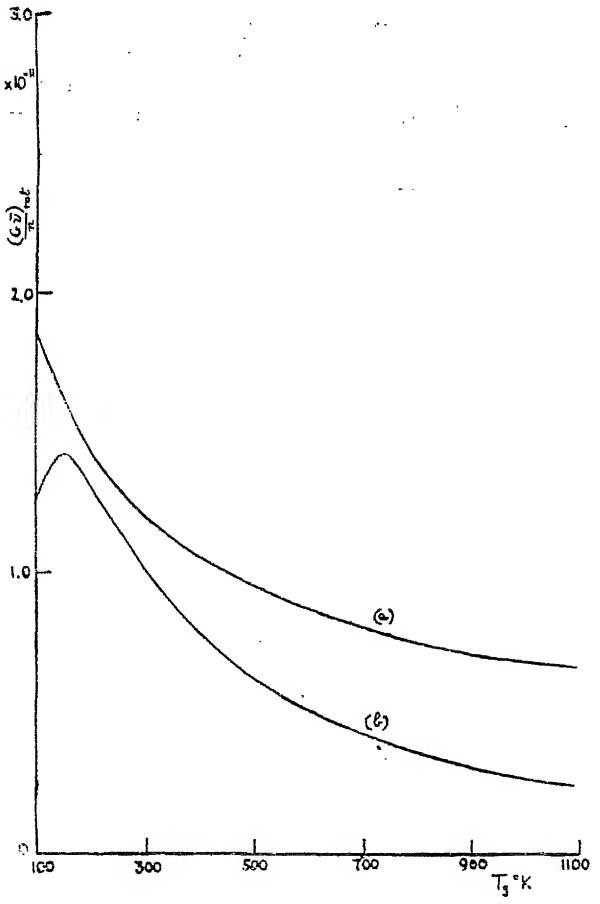

Fig. 3. Energy loss parameter $\frac{(G\bar{\nu})_{rot}}{n}$ plotted against gas temperature.

Curve (*a*) : Present values, with $|q| = 1{\cdot}01$

(*b*) : Values due to Huxley (1959).

unsatisfactory except at the lowest temperatures. We believe that the theoretical values are to be preferred since $\left(G\bar{\nu}\right)_{rot}$ is insensitive to uncertainties in the cross sections.

The elastic contribution to $G\bar{\nu}$ is

$$\left(G\bar{\nu}\right)_{el} = \frac{8m\bar{\nu}}{3M} \tag{31}$$

and adding (31) to $(G\bar{\nu})_{rot}$ gives the values of $G\bar{\nu}$ listed in the table. Values of the parameter G are also given since they are useful in some applications.

6. VALIDITY OF THE ENERGY LOSS FORMULA

The energy loss formula (1), which is used for the analysis of radio wave interactions (the Luxembourg effect), is an approximation to (28) and is valid only for a restricted range of temperature differential $(T_e - T_g)$. A comparison of (28) with $(G\bar{\nu})_{rot} \times (\bar{E} - E_g)$ as a function of $T_e - T_g$) is made in figure 4 for $T_g = 300°K$. The linear approximation becomes inaccurate when the difference between the electron and gas temperatures becomes greater than the gas temperature.

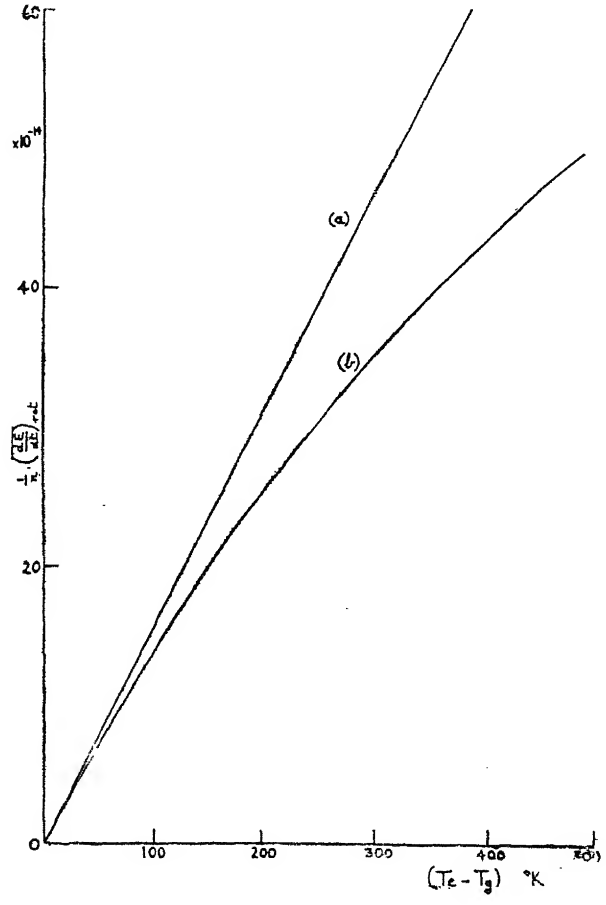

Fig. 4. $\frac{1}{n}\left(\frac{\overline{dE}}{dt}\right)_{rot}$ plotted against $(T_e - T_g)$, at $T_g = 300°K$.
Curve (a) : From the approximation $\frac{1}{n}(G\bar{\nu})_{rot}(\bar{E} - E_g)$
Curve (*b*) : From accurate formula (28).

TABLE

Values of $G\bar{\nu}$ and G for various temperatures
$|q|$ was taken as 1·01, in agreement with
Frost & Phelps (1961).*

$T°K$	100	200	300	400	500	700	1000
$G\bar{\nu} \times 10^{-3}$	3·98	3·10	2·62	2·34	2·13	1·87	1·63
$G \times 10^{3}$	13·1	5·08	2·87	1·92	1·40	0·877	0·535

* The number density of N_2 used is $2{\cdot}1 \times 10^{14}$ cm^{-3}.

ACKNOWLEDGMENTS

The research reported has been sponsored by the Air Force Cambridge Research Center, Geophysics Research Directorate, of the Air Research and Development Command, U. S. Air Force, through its European Office, under Contract No. AF 61 (052)-131.

One of us (R. J. M.) is indebted to the Ministry of Education, Northern Ireland, for a research grant.

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PRODUCTION OF NO^+ IN A MASS SPECTROMETER CONTAINING NITROGEN AND OXYGEN

By

J. F. PAULSON

Air Force Cambridge Research Laboratories, Bedford, Massachusetts, U. S. A.

and

R. L. MOSHER

Device Development Corporation, Weston, Massachusetts, U. S. A.

INTRODUCTION

The study of gas phase reactions between ions and neutral atoms or molecules is of increasingly wide interest because of the possible importance of these reactions in such diverse fields as radiation chemistry, atmospheric physics, and the physics of electrical discharges in gases. The most co nmonly used technique for studying ion-molecule reactions has been the production of ions by electron bombardment in the ion source of a mass spectrometer and the analysis of the primary ions (*i. e.* those produced by electron bombardment directly or by subsequent unimolecular dissociation of these ions) and of the secondary ions (*i. e.* those produced upon collision of the primary ions with neutral atoms or molecules in the ion source) in the mass spectrometer. More refined techniques, e. g. the use of two mass spectrometers coupled together, the first to produce a mass analyzed ion beam and the second to determine the composition of the ion-molecule reaction products, have occasionally been used.[1]

In general, three or sometimes four parameters are varied in the study of an ion-molecule reaction by mass spectrometry. The ionizing voltage is varied so as to determine the ionic reactant; the ionic product of the reaction will in general have the same appearance potential as that of the ionic reactant. Variation of the repeller potential or draw out potential will change both the residence time of the ions in the source and their energy distribution. The pressure in the source may be varied. In the simplest case of an ion-molecule reaction between a neutral and its corresponding ion or an ionic fragmentation product of its parent ion, the rate of formation of secondary ions will be proportional to the second power of the pressure, since both the primary ion concentration and the neutral concentration are varied. The fourth parameter which may be varied is the ionizing current. For a given pressure and repeller potential, this parameter determines the concentration of ions in the source; hence the rate of production of secondary ions is proportional to the ionizing current, so long as only a small fraction of all the primary ions is consumed in ion-molecule reactions.

Although the simpler hydrocarbons, the rare gases, and hydrogen have been the subjects of several ion-molecule reaction studies, little attention has been paid to reactions involving the more abundant ions of the atmosphere, *e. g.* O^+, O_2^+, NO^+, N^+, and N_2^+. Of great interest in studies of the dynamics of the earth's

atmosphere are reactions producing the nitric oxide positive ion, as this is one of the predominant positive species in the ionosphere[2,3]. At the time the experiments discussed in this paper were begun, the only experimentally determined rate constant available in the literature for an ion-molecule reaction producing NO^+ was that of Potter[4], for the process.

$$O^+ + N_2 \longrightarrow NO^+ + N$$

The value was $k = (1{\cdot}0 \pm 0{\cdot}25) \times 10^{-9} cm^3/$ molec. sec. This extraordinarily high rate constant has become the subject of considerable discussion and controversy[5,6,7,8]. Lower values of the rate constant for the same reaction were deduced from ionospheric data by Bates and Nicolet[7], by Yonezawa *et al*[9], and by Danilov[10]. The values obtained by these workers, together with some recent experimental results, are given in Table I and are seen to range from about 10^{-9} to less than 10^{-13} $cm^3/$ molec. sec. The work described in this paper was begun with the hope of resolving the controversy on this rate constant and of obtaining the rate constants for other ion-molecule reactions producing NO^+.

TABLE I

Rate Constants for $O^+ + N_2 \rightarrow NO^+ + N$

k ($cm^3/$ *sec.*)	*Remarks*	*Reference*
1×10^{-9}	thermal O^+	4
$9{\cdot}7 \times 10^{-10}$	EHT*	16
$< 2 \times 10^{-10}$	$< 0{\cdot}5$ eV O^+	this work
$\sim 1{\cdot}5 \times 10^{-10}$	4-5 eV O^+	17
$1{\cdot}0 \times 10^{-10}$	ionosphere	10
$2{\cdot}9 \times 10^{-11}$	ionosphere	9
$< 6{\cdot}7 \times 10^{-11}$	$<$ 1 ev O^+	18
$2{\cdot}7 \times 10^{-11}$	thermal O^+	19
$4{\cdot}7 \times 10^{-12}$	thermal O^+	20
$< 10^{-13}$	ionosphere	7

EXPERIMENTAL

A Consolidated Electrodynamics Corporation Model 21-103 mass spectrometer was used in these experiments. The instrument was modified slightly by the use of battery powered repellers and a rhenium filament. Electrostatic scanning was used, except for a few runs in which magnetic scanning was used in order to determine the mass discrimination effect. All results have been corrected to accord with those obtained from magnetic scanning.

*Calculated from the formula given by Eyring, Hirschfelder, and Taylor (reference 16)

Nitrogen and oxygen at pressures up to about $0{\cdot}5 \times 10^{-3}$ torr and in various ratios were admitted to the ion source from a 3-liter reservoir. The concentration of gas in the ion source was determined by applying a negative bias of 40 V to the repellers and measuring the collected ion current. Ionization cross sections for nitrogen and oxygen were taken from the literature[11]. The technique for determining concentrations in the source has been described by Field, Franklin, and Lampe[12]. An ion gauge was used to estimate gas pressure and was calibrated for various pressures and mixtures of nitrogen and oxygen in the source.

Because the analyzer tube is not differentially pumped in the CEC 21-103 mass spectrometer, scattering and charge exchange effects in this region are serious sources of error at pressures above about 10^{-5} torr. Calibration curves were obtained by analyzing various mixtures of N_2, O_2 and NO at several pressures.

Repeller voltages from 1 to 40 V were used, corresponding to potential gradients from 4 to 160 V/cm. Since the perpendicular distance from the midpoint of the electron beam, assumed to be undeflected by the repeller field, to the first accelerating slit was 0·13 cm, maximum ion energies ranged from about 0·5 V with a repeller potential of 1 V to about 20 V with a repeller potential of 40 V. Accelerating voltage field penetration effects were neglected.

An ionizing current of 10 μ amp was generally used, and the ionizing voltage was 70 V. The ion source was maintained at 250° C. Matheson Research Grade nitrogen and oxygen were used in most runs, but no appreciable difference in the rate constant for NO^+ formation was observed when laboratory air was passed through a trap at —196° C and admitted to the mass spectrometer. Matheson nitric oxide was passed through Ascarite to remove NO_2 and trap-to-trap distilled on a vacuum line, the middle third being retained for analysis.

RESULTS

PRESSURE STUDIES

Nitrogen and oxygen at total pressures up to about 5×10^{-4} torr and in various ratios between $\frac{[N_2]}{[O_2]} = \frac{4}{1}$ and $\frac{1}{1}$ were admitted to the ion source. A peak at m/e 30 was observed and found to be in excess of that due to $N^{15}N^{15}$. Neither N_2O^+ nor NO_2^+ was observed. However, contributions to m/e 44 (N_2O^+) from CO_2 present as an impurity and in the background spectrum would have obscured the production of small amounts of N_2O^+.

REPELLER STUDIES

The results of varying the repeller voltage from 1 to 40 V are shown in Fig. 1. An increase in repeller potential causes several effects, which may be competitive. Thus, the transmission of the mass spectrometer is at first increased, since a larger fraction of the ions is removed from the source rather than being neutralized by wall collisions. At still higher repeller potentials the single focusing mass spectrometer is unable to focus the energetic ions emerging from the source, and the peak height decreases. These effects are seen in the curves for the primary ions in

Fig. 1. The form of the curve is clearly mass dependent. The interpretation of peaks due to secondary ions must, in addition to the above effects, also consider the effects of increased primary ion energy and decreased residence time upon the rate

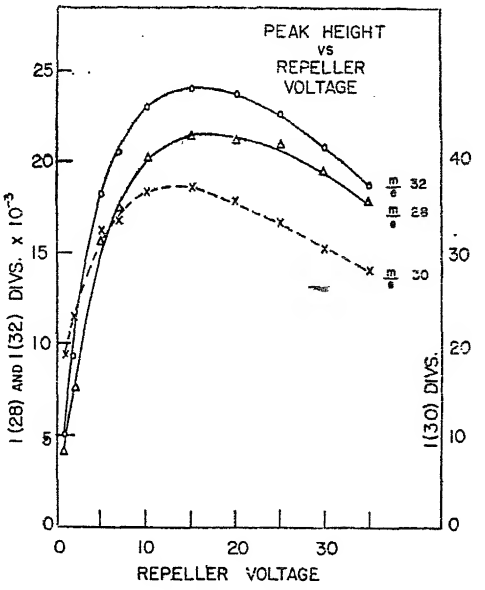

Fig. 1. Peak height vs. repeller voltage.

of a given reaction. The rate of formation of product of an ion-molecule reaction is given by

$$R = k\, n_1\, n_2$$

$$= \sigma\, v\, n_1\, n_2$$

where k is the rate constant, n_1 is the number density of the ionic reactant, n_2 is the number density of the neutral reactant, σ is the reaction cross-section, and v is the relative velocity of the ionic and neutral reactants, which may be taken to be simply the velocity of the ionic species. As the repeller potential is increased, the steady state concentration of neutral species is unchanged, whereas that of ionic species decreases, varying inversely as the square root of the repeller potential, to a first approximation. The velocity of the reactant ions increases as the square root of the repeller potential. Hence these effects cancel. The effect upon the reaction cross-section is in general unknown, but experimental evidence[13] on exothermic reactions indicates that the reaction cross-section varies inversely as the repeller potential, often as the inverse first power.

In a plot of peak height against repeller potential, then, the effect of increasing transmission is superimposed upon that of decreasing reaction cross-section. It is not generally possible to predict quantitatively the overall effect, although it may be expected that a peak due solely to an ion-molecule reaction will increase more slowly at low repeller potentials and decrease more rapidly at high repeller potentials than will a peak due to a primary ion of similar mass-to-charge ratio. In fact,

the effects of decreasing reaction cross-section and primary ion concentration often far outweigh that of increasing transmission, and the secondary ion peak will decrease monotonically from the lowest attainable repeller potential.

In Fig. 1, the curve of the ion current of m/e 30 indicates less change in the ion current over the range from 1 to 15 volts repeller potential than might be expected if there were no production of NO^+ by ion-molecule reactions. However, other interpretations are possible, *e.g.* that NO, formed on or near the hot filament, is ionized and then subjected to a different repeller field than are ions produced from a gas admitted to the ion source from the gas reservoir.

IONIZING VOLTAGE STUDIES

Fig. 2 shows the results of varying the ionizing voltage. The first ionization potential of nitrogen, 15·60 ev[14], was taken as the standard for calibrating the

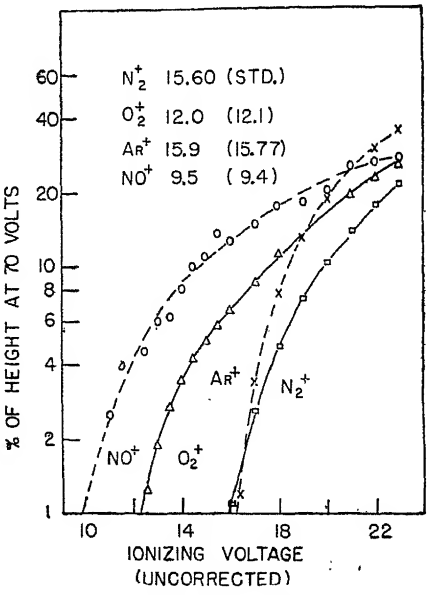

Fig. 2. Ionizing voltage vs. peak height.
Ionization potentials in parentheses are taken from Reference 13.
o NO^+; $\triangle O_2^+$; o N_2^+; × Ar^+

electron energy. Lossing's method[15] was used, except that the peak heights at 70 V, rather than at 50 V, were taken as the reference point. It is obvious that some nitric oxide is produced as the neutral species in the mass spectrometer, since the appearance potential of the m/e 30 peak agrees with the accepted value[14] of the first ionization potential of nitric oxide to within experimental error. If neutral or ionized nitrie oxide were produced solely as the result of an ion-molecule reaction, its appearance potential would be expected to correspond to that of the ionic reactant. All such appearance potentials in nitrogen and oxygen lie well above that observed for the NO in these experiments. However, if nitric oxide were produced by two mechanisms, one of which involved no reactants requiring more than about 9·25 ev for their formation, and one of which involved an ionic reactant, then the ionizing voltage corresponding to 1% of the ionization efficiency at 70 V

would be greater than would be observed when pure NO was admitted to the ion source. Unfortunately, the region of low ionization efficiency is also that involving the largest experimental errors, as the ionizing electron energy spread is relatively large and the observed NO^+ peak heights are very small in this region. If, say, only 10% of the NO^+ observed at 70 V were due to an ion-molecule reaction, then at 9·25 V the ionization efficiency would be about 0·9% rather than 1·0%. From the ionizing voltage studies, then, we can conclude only that some neutral nitric oxide is produced from neutral N_2 and O_2 or perhaps from species that require less than 9·25 ev for their production from N_2 or O_2.

DISCUSSION

For the purpose of discussion, several conceivable ion-molecule reactions leading to the production of nitric oxide are given below, together with the energy evolved (positive sign) or absorbed (negative sign), in each reaction, when this quantity can be calculated.

1. $N_2^+ + O_2 \rightarrow NO^+ + NO + 4{\cdot}5$ eV
2. $N_2^+ + O \rightarrow NO^+ + N + 3{\cdot}1$ eV
3. $N_2^+ + O \rightarrow NO + N^+ - 2{\cdot}2$ eV
4. $N^+ + O_2 \rightarrow NO^+ + O + 6{\cdot}7$ eV
5. $N^+ + O_2 \rightarrow NO + O^+ + 2{\cdot}3$ eV
6. $O_2^+ + N_2 \rightarrow NO^+ + NO + 1{\cdot}1$ eV
7. $O_2^+ + N \rightarrow NO^+ + O + 4{\cdot}3$ eV
8. $O_2^+ + N \rightarrow NO + O^+ + 0{\cdot}0$ eV
9. $O^+ + N_2 \rightarrow NO^+ + N + 1{\cdot}2$ eV
10. $O^+ + N_2 \rightarrow NO + N^+ - 4{\cdot}1$ eV
11. $N^+ + O \rightarrow NO^+ + h\nu$
12. $O^+ + N \rightarrow NO^+ + h\nu$

Reactions 2, 3, 7, 8, 11, and 12 are not considered further here as they involve collisions between species both of which are present in low concentration in the ion source. Reactions 3 and 10 are endothermic and are probably not important at low ion energies.

If it is assumed that the nitric oxide observed in this work is produced at least partly by reaction between neutral species, then only upper limits for the rate constants for reactions 1, 4, 6 and 9 may be calculated. The applicable equation is

$$k = \frac{i_2}{i_1 n I}$$

where k is the rate constant in cm^3/ molec. sec., i_2 is the peak height of the secondary ions (NO^+), i_1 is the peak height of the reactant ions, n is the number density of neutral reactant species and T is the residence time of the reactant ions in the source. The residence times were calculated from the formula given by Field, Franklin, and Lampe[12]. The upper limits given in Table II are for reactant

TABLE II

Upper Limits for k_1, k_4, k_6, and k_9

$n_{N_2} \times 10^{-13}$ molecules per cm^3	$n_{O_2} \times 10^{-13}$	$k_1 \times 10^{10}$	$k_4 \times 10^{10}$ cm^3/molec. sec.	$k_6 \times 10^{10}$	$k_9 \times 10^{10}$
0·8	0·2	0·55	4·2	0·49	2·7
1·6	0·4	0·36	2·8	0·31	1·7
3·8	0·9	0·31	2·4	0·28	1·5
4 9	1·2	0·30	2·3	0·27	1·5
6·4	1·6	0·44	3·4	0·39	2·1
3·8	3·8	0·42	3·2	0·38	2·2
4·1	3·1	0·43	3·3	0·41	2·2

ions of maximum energy 0·5 eV and are calculated on the assumption that the respective reaction is solely responsible for all the NO^+ observed. Because the rate constants for different ion-molecule reactions may differ by several orders of magnitude, we do not believe it is possible to eliminate from consideration any reactions involving, say, N^+ and N_2^+ by admitting to the ion source a sample containing only a small mole fraction of nitrogen and a large one of oxygen.

Calculations of the rate constants for reactions 1, 4, 6, and 9 based on the theory of Eyring, Hirschfelder, and Taylor[16] give values very close to^{-9} cm^3/ molec. sec. It would be of interest to know whether the difference between this theoretical value and the upper limits given in Table II are due to activation energy effects. not considered in deriving the theory. If there were an activation energy requirement, then we might expect that the rate constant of the ion-molecule reaction would be strongly dependent upon the ion kinetic energy, *i. e.* upon the repeller potential. Such an effect would of course by obscured in the present work by the production of NO in processes other than ion-molecule reactions.

Since this work was first reported, some other recent values for k_9 have come to our attention. These are listed in Table I, together with some previously reported values for comparison. It is clear that interpretation of ionospheric electron densities based upon a value of $k_9 = 1 \times 10^{-8}$ cm^3/ molec. sec. must be discarded, even though the rate constant is still not well established.

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INELASTIC ION-ATOM COLLISIONS : TOTAL IONIZATION AND CHARGE TRANSFER MEASUREMENTS IN THE ENERGY RANGE 100-500 keV

By

J. B. HASTED

University College, London, England

ABSTRACT

Cross-sections for total positive ion production and for transfer plus stripping processes in the energy region 50-500 keV are presented for Ar^+ Ar, Ar^+ Ne, Ar^+ He, Ar^+ Kr, Ne, $^+$ Ne. The total positive ion cross-section is measured with a new technique, in which the electrons are suppressed with a magnetic field parrallel to the projectile ion beam; discrepancies between measurements of total electron production are found to disappear.

In this paper we present the results of total ionization and charge transfer measurements in the energy range 100-500 keV for the collisions: Ne^+ Ne, Ar^+ Ar, Ar^+ Ne, Ar^+ He, Ar^+ Kr. These have have taken at University College London by A. R. Lee, J. V. Ireland, H. B. Gilbody and myself, using the well established method collection of charge at plates which maintain a uniform electric field transversely to the ion beam (1).

TOTAL CHARGE COLLECTION AT HIGH ENERGIES

The collision between a singly charged positive ion and an atom may give rise to ionizing collisions of the general type:

$$A^+ + B \rightarrow A^{m+} + B^{n+} + (m+n-l)\ e \quad \text{(process } 10/mn\text{)}$$

These may be classified as exchange collisions, in which the ion loses its charge—in general $10/0n$; and ionizing collisions in which $m \geqslant 0$. The simplest exchange collision is charge transfer 10/01, and where $n > 1$ we may imagine that the collision, $10/0n$, although ionizing, is partly exchange; we shall call collisions of this type, such as 10/02, "transfer ionization"; another designation, "ionization with capture", has been suggested by Fedorenko. The charge transfer process is often referred to as "electron capture", and as "charge exchange", but the latter may be misleading because of confusion with the electron exchange interaction or process. Ionizing collisions in which the electrons are driven from the projectile ion are referred to as "stripping".

In the collection of the total 'slow' charge produced in these collisions, attempts have been made to collect:

1. The total electron current produced. This is achieved by measuring the total negative current to the positive electrode of the system maintaining the transverse electric field. Secondary electrons arising from the impact of slow positive ions upon the negative collecting electrode must be eliminated or at least estimated. The method of correction worked out by Keene (2) has been replaced by simple suppression technique in which a negatively charged grid of known transparency is placed in front of the positive ion collector (1). The cross-section calculated from electron current measurements is:

$$\sigma_e = \sum_{m,n} (m+n-1)\ {}_{10}\sigma_{mn}$$

$$= \sum_{n} (n-1)\,{}_{10}\sigma_{0n} + \sum_{n} n\,{}_{10}\sigma_{1n} + \sum_{\substack{m,n \\ m>1}} (m+n-1)\,{}_{10}\sigma_{mn}$$

transfer plus transfer ionization | ionization | stripping

2. The total positive and negative charge produced. This is achieved by measuring simultaneously the currents produced at both positive and negative collecting electrodes of the system maintaining the transverse electric field. Since the ionization of the target particle produces equal amounts of positive and negative charge, which balance out, this measurement covers only exchange processes, plus, as sufficiently high energies, stripping processes. It was originally devised to measure charge transfer. At sufficiently high energies stripping may be more probable than transfer so that the current becomes negative instead of positive. We shall use the convention that σ_{cs} refers to the cross-section when the charge transfer exceeds the stripping, and σ_{sc} to the cross-section when the stripping exceeds the charge transfer :

$$\sigma_{cs} = \sum_{m,n} (1-m)\,{}_{10}\sigma_{mn} = \sum_{n} {}_{10}\sigma_{0n} - \sum_{\substack{m,n \\ m>1}} (m-1)\,{}_{10}\sigma_{mn}$$

transfer plus transfer ionization | part of stripping

3. The total positive ions produced. There is obviously a choice as to which two of these three measurements are made. In earlier work it was considered easier to measure electron currents, partly because it is easier to confine electrons in magnetic field, partly because the measurement of total positive ions only gives the purely ionizing collision cross-section as a difference. However, more serious discrepancies appeared between the measurements of different workers than in the charge transfer measurements, and it was thought that these might arise from such stray electrons as those produced by surface collisions of metastable atoms formed in collisions. Stray ions are notoriously rarer than stray electrons, so it was decided to make measurements of the cross-section for total positive ion production :

$$\sigma_{+} = \sum_{m,n} n\,{}_{10}\sigma_{mn} = \sum_{n} n\,{}_{10}\sigma_{0n} + \sum_{n} n\,{}_{10}\sigma_{1n} + \sum_{\substack{m,n \\ m>1}} n\,{}_{10}\sigma_{mn}$$

transfer plus transfer ionization | ionization | part of stripping

so that $$\sigma_{e} = \sigma_{+} - \sigma_{cs}$$

This was achieved by Fedorenko by means of a measurement of the total positive current to the negative collecting electrode of the system maintaining the transverse electric field, the secondary electrons from both electrodes being suppressed by grids. This has the disadvantage that the transparency of the grid in front of the negative collecting electrode must be known; use has therefore been made by Gilbody *et al.* of a magnetic field parallel to the incident beam, which not only suppresses the secondary electrons but also the electrons formed by the ion-atom collisions, causing them to travel trochoidally along the incident beam,

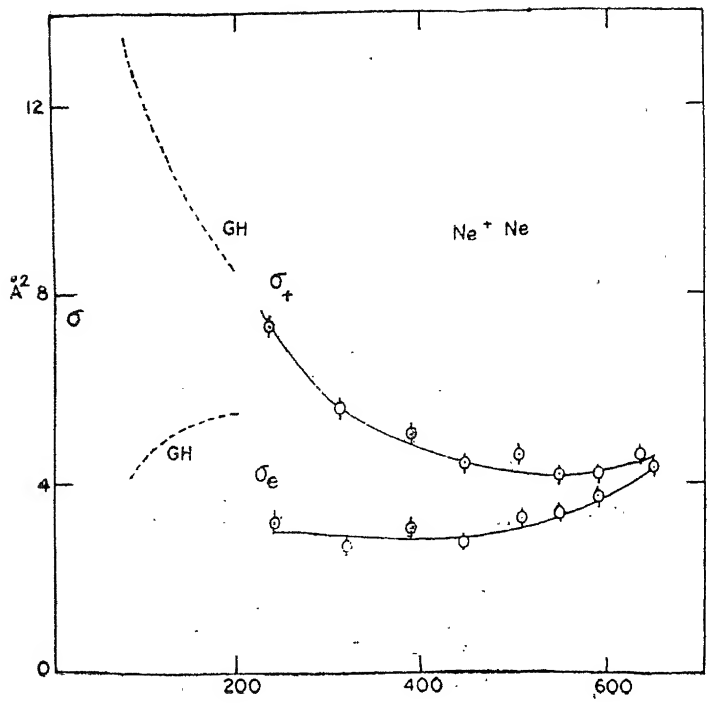

Fig. 1

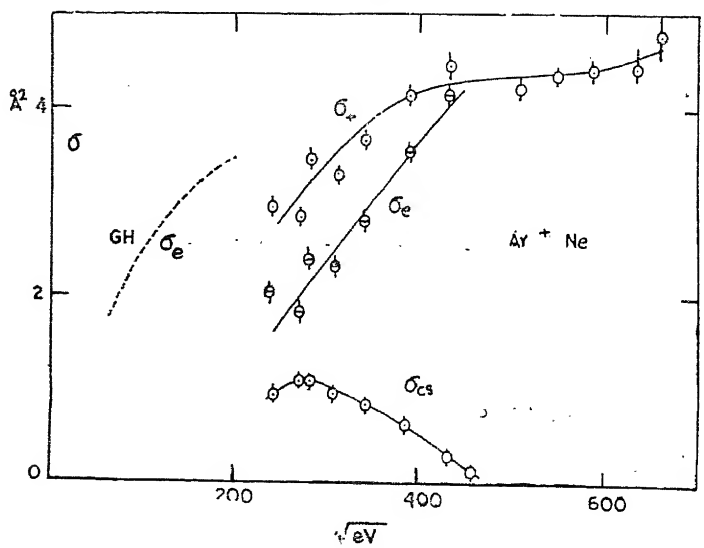

Fig. 2

σ_+, σ_e, σ_{cs} in units of 10^{-16} cm^2 as functions of incident ion energy, in (electron-volts)$^{\frac{1}{2}}$.
Present results represented as full curve with experimental points.
GH, dashed curves, Gilbody and Hasted (1)

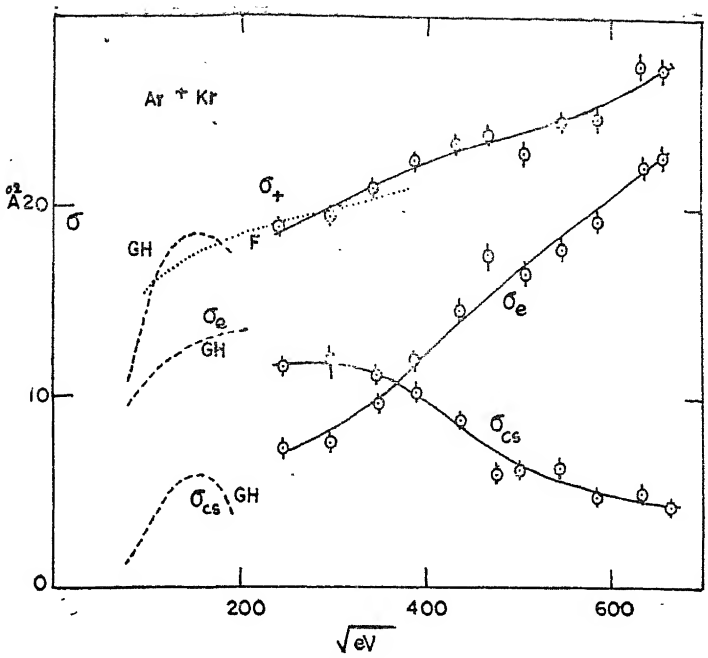

Fig. 3

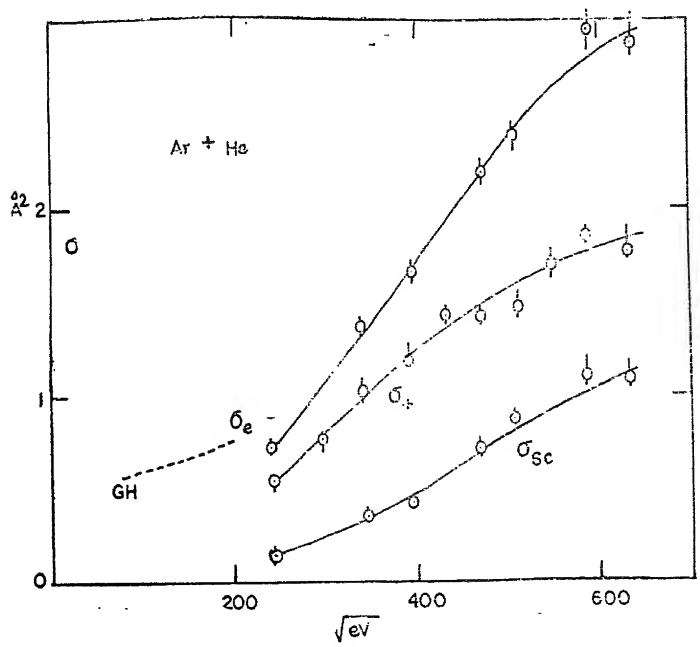

Fig. 4

σ_+, σ_e, σ_{cs} in units of 10^{-16} cm^2 as functions of incident ion energy in (electron-volts)$^{\frac{1}{2}}$
Present results represented as full curve with experimental points.
GH, dashed curves, Gilbody and Hasted (1)
F, dotted curves, Afrosimov and Fedorenko (3)

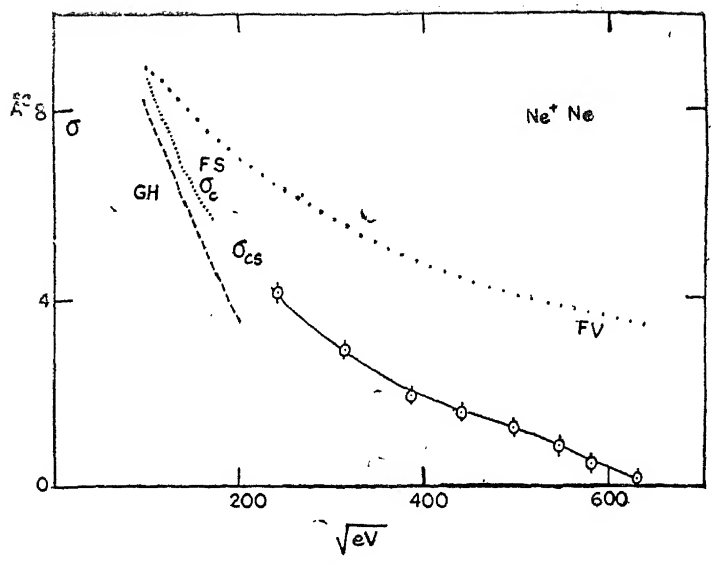

Fig. 5

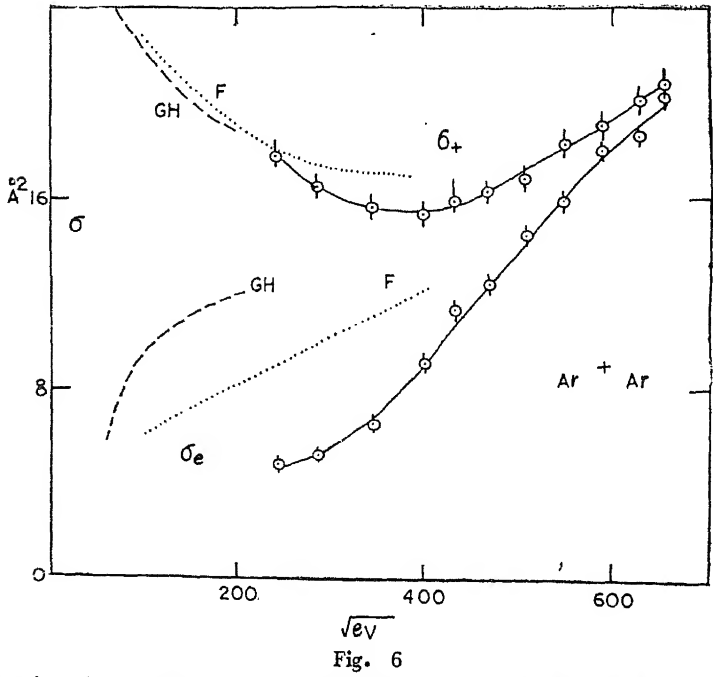

Fig. 6

σ_+, σ_e, σ_{cs}, in units of 10^{-16} cm^2 functions of incident ion energy, in (electron-volts)$^{\frac{1}{2}}$. Present results represented and full curve with experimental points.

GH, dashed curves, Gilbody and Hasted (1)

F, dotted curves, Afrosimov and Fedorenko (3)

FS, dotted curves, Flaks and Solov'ev (4)

FV, dotted curves, Firsov (5) calculations.

Under these conditions the small number of higher energy electrons are more easily controlled than with the larger transverse fields otherwise necessary. It is significant that the discrepancies found in σ_e measurements largely disappear with the newer technique of σ_+, σ_{cs} measurement.

It is important to realise that at high energies the cross-sections of theoretical importance do not emerge easily from these measurements. For a knowledge of the exchange cross-sections an independent measurement of stripping must be made, and even then a separation of transfer from transfer ionization cannot be made. However the total ionization cross-section, which can be compared, for example, with statistical ionization theory, is clearly σ_d, now a difference measurement, but probably more accurate than previously. It should be noted that σ_+ is not a purely ionization collision; also that the 'stripping' process, as defined in the Equations, includes some 'stripping with target ionization". A varying amount of stripping and of transfer ionization is included in the three cross-sections.

In all measurements the electric and magnetic fields were varied until no further change of collected current accompanied this variation ("saturation conditions"); a linear variation of collected current with collision chamber gas pressure was established for each measurement. The details of ion source and accelerator, van der Graaff generator, electrostatic and magnetic analysis will be given in a future publication.

The results of these measurements are shown are functions of ion energy in Figures 1-7, together with comparisons with existing data.

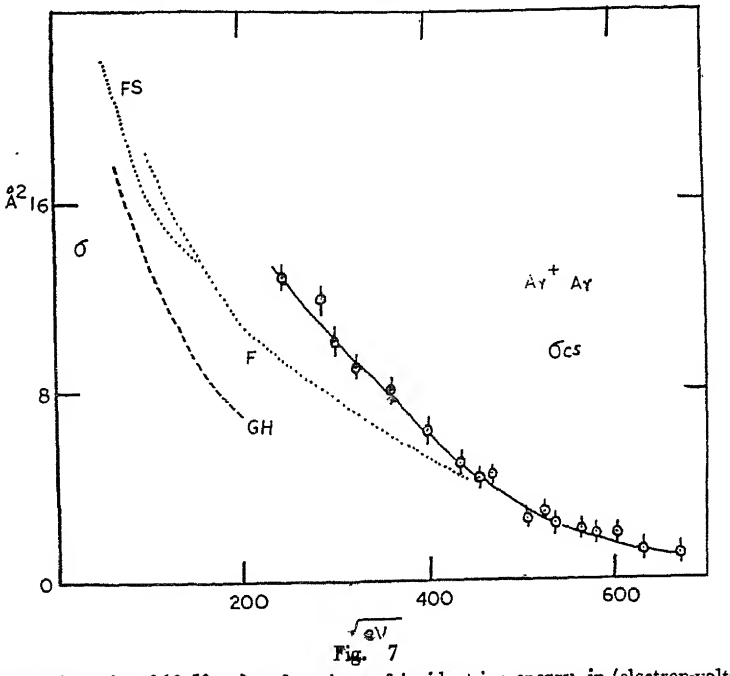

Fig. 7

σ_+, σ_d, σ_{cs} in units of 10^{-16} $cm.^2$ as functions of incident ion energy, in (electron-volts)$^{\frac{1}{2}}$. Present results represented as full curve with experimental points.

GH, dashed curves, Gilbody and Hasted (1)

F, dotted curves, Afrosimov and Federenko (3)

FS, dotted curves, Flaks and Solov'ev (4)

Unfortunately the absence of "stripping" cross-section data make a detailed discussion premature at this stage. It should be noted, however, that if the stripping cross-sections are assumed to be small, an application of the principle of detailed balancing can be made to the charge transfer data. Cross-sections for the reverse processes have since been measured, and the results are in conformity with this principle. This encourages confidence in the accuracy of the data and the soundness of the axial magnetic field technique.

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A SIMPLIFICATION OF THE SECOND BORN APPROXIMATION

By

B. L. MOISEIWITSCH

Department of Applied Mathematics, The Queen's University of Belfast, N. Ireland

ABSTRACT

It is shown that the simplification of the second Born approximation first suggested by Massey and Mohr is equivalent to taking an infinite value for the polarizability of the target system. An alternative simplified form for the second Born approximation is proposed which corresponds to choosing the correct value for the dipole polarizability.

1. INTRODUCTION

A simplified form for the second Born approximation has been applied to the scattering of electrons by atoms by Massey and Mohr (1934) and also by Rothenstein (1954) and by Moiseiwitsch and Williams (1959). It is now known that this simplification leads to considerable error (Bates 1958; Kingston, Moiseiwitsch and Skinner 1960; Kingston and Skinner 1961). The purpose of this paper is to clarify the reason for the breakdown of the Massey and Mohr approximation and to propose an alternative simplification of the second Born approximation which is less open to objection.

2. SECOND BORN APPROXIMATION

It is convenient to consider the special case of the scattering of charged particles by hydrogen atoms. This can be described in terms of the asymptotic solution of the infinite set of coupled differential equations

$$(\nabla^2 + k_p^2) F_p(r) = \frac{2M}{\hbar^2} \sum_q V_{pq}(r) F_q(r) \tag{1}$$

where

$$V_{pq}(r_1) = \int \phi_p^*(r_2)\, V(r_1, r_2)\, \phi_q(r_2)\, dr_2 \tag{2}$$

and

$$k_p^2 = \frac{2M}{\hbar^2} (E - \epsilon_p), \tag{3}$$

E being the total energy and M the reduced mass of the whole system, $\phi_p(r)$ being the eigenfunction and ϵ_p the eigenenergy of the pth state of a hydrogen atom, and $V(r_1, r_2)$ being the interaction potential between the incident particle and the atom.

Denoting the initial state of the hydrogen atom by $p=0$, the asymptotic form of $F_p(r)$ for large values of r is given by

$$F_0(r) \sim \exp ik_0 \hat{n} \cdot r + r^{-1} f_0(\theta, \phi) \exp ik_0 r \tag{4}$$

$$F_p(r) \sim r^{-1} F_p(\theta,\phi) \exp ik_p r \qquad (p \neq 0) \tag{5}$$

where $\hat{n}_0$ is the unit vector in the direction of the incident particle.

We first consider the case of elastic scattering in which after the collision the hydrogen atom is left in the state $p = 0$ and the scattered particle is travelling in the direction of the unit vector $\hat{n}$. Then the second Born approximation to the scattering amplitude $f_0(\theta,\phi)$ is given by

$$f_0 = f_{B1} + f_{B2} \tag{6}$$

where

$$f_{B1} = -\frac{1}{4\pi}\left(\frac{2M}{\hbar^2}\right)\int \exp ik_0 (\hat{n}_0 - \hat{n}).\, r\ V_{00}(r)\, dr \tag{7}$$

and

$$f_{B2} = \frac{1}{4\pi}\left(\frac{2M}{\hbar^2}\right)^2 \sum_q \iint \exp ik_0 (\hat{n}_0 . r_1 - \hat{n} . r_1')\ V_{q0}^*(r_1')\ V_{q0}(r_1) \times \frac{\exp ik_q |r_1 - r_1'|}{4\pi |r_1 - r_1'|}\, dr_1\, dr_1', \tag{8}$$

f_{B1} being just the first Born approximation to the scattering amplitude.

In the present paper we are mainly concerned with polarization, *i. e.* with the influence of virtual intermediate states q other than the initial state $q = 0$. Denoting by f_{B2}^P that part of expression (8) for f_{B2} which corresponds to polarization, we have

$$f_{B2}^P = \frac{1}{4\pi}\left(\frac{2M}{\hbar^2}\right)^2 \sum_{q \neq 0} \iint \exp ik_0 (n_0 . r_1 - \hat{n} . r_1')\, V_{q0}^*(r_1')\, V_{q0}(r_1) \times \frac{\exp ik_q |r_1 - r_1'|}{4\pi |r_1 - r_1'|}\, dr_1\, dr_1' \tag{9}$$

Now for $k_o a_o << 1$ we may put †

$$(\nabla^2 + k_q^2) \left\{ \exp (ik_o \hat{n}_o . r) V_{qo} (r) \right\} \cong (k_q^2 - k_o^2) \exp (ik_o \hat{n}_o . r) V_{qo} (r) \quad (10)$$

since $\nabla^2 V_{qo}$ may be neglected compared to V_{qo}, and so we obtain

$$f_{B2}^{p} \cong \frac{1}{4\pi} \left(\frac{2M}{\hbar^2} \right)^2 \sum_{\substack{q \\ \neq o}} \iint \frac{(\nabla_1^2 + k_q^2)}{k_q^2 - k_o^2} \left\{ \exp (ik_o \hat{n}_o . r_1) V_{qo} (r_1) \right\} \quad (11)$$

$$\times \exp (- ik_o \hat{n} . r_1') V_{qo}^{*} (r_1') \frac{\exp ik_q | r_1 - r_1' |}{4\pi | r_1 - r_1' |} dr_1 dr_1'$$

which, on using Green's theorem, becomes

$$f_{B2}^{p} \cong \frac{1}{4\pi} \left(\frac{2M}{\hbar^2} \right)^2 \sum_{\substack{q \\ \neq o}} \iint \exp ik_o (\hat{n}_o . r_1 - \hat{n} . r_1') \frac{V_{qo}^{*} (r_1') V_{qo} (r_1)}{k_q^2 - k_o^2}$$

$$\times (\nabla_1^2 + k_q^2) \frac{\exp ik_q | r_1 - r_1' |}{4\pi | r_1 - r_1' |} dr_1 dr_1' . \quad (12)$$

Since

$$(\nabla_1^2 + k_q^2) \frac{\exp ik_q | r_1 - r_1' |}{4\pi | r_1 - r_1' |} = - \delta (r_1 - r_1') \quad (13)$$

and

$$\frac{\hbar^2}{2M} (k_q^2 - k_o) = \epsilon_o - \epsilon_q \quad (14)$$

it follows that

$$f_{B2}^{p} \cong - \frac{1}{4\pi} \left(\frac{2M}{\hbar^2} \right) \int \exp ik_o (\hat{n}_o - \hat{n}) . r_1 \sum_{\substack{q \\ \neq o}} \frac{V_{qo}^{*} (r_1) V_{qo} (r_1)}{\epsilon_o - \epsilon_q} dr_1 . \quad (15)$$

---

† Note that k_q is imaginary if $k_o^2 < \frac{2M}{\hbar^2} (\epsilon_q - \epsilon_o)$.

Thus for $k_o\, q_o << 1$ we have reduced expression (9) for J^{P}_{B2} into the form of a first Born approximation integral in which the matrix element of the interaction potential is replaced by

$$\sum_{\substack{q \\ \neq o}} \frac{V^{*}_{q\,o}(r)\; V_{qo}(r)}{\epsilon_o - \epsilon_q} \,. \tag{16}$$

This expression is just the second order contribution to the interaction energy which arises from the application of perturbation theory.

Now according to the approximation of Unsöld (1927) we may replace (16) by

$$\frac{1}{\triangle E} \sum_{\substack{q \\ \neq o}} V \quad (r)\; V_{qo}(r) \tag{17}$$

where the constant $\triangle E$ is to be chosen so that the first term of the expansion of (17) in powers of $1/r$ is the same as that for expression (16). Dalgarno and Lewis (1956) have shown that for a particle of charge Ze situated at a distance r from the nucleus of a hydrogen atom, (16) can be expanded in the form

$$-\frac{(Ze)^2}{2a_o} \sum_{l=1}^{\infty} \left(\frac{a_o}{r}\right)^{2l+2} \frac{(2l+2)!}{2^{2l}+1} \frac{l+2}{l\,(l+1)} \tag{18}$$

while expression (17) can be written in the form

$$\frac{1}{\triangle E} \left(\frac{Ze^2}{2a_o}\right)^2 \sum_{l=1}^{\infty} \left(\frac{a_o}{r}\right)^{2l+2} \frac{(2l+2)!}{2^{2l-1}} \frac{1}{2l+1} \tag{19}$$

Hence the leading terms of (18) and (19) are identical if we put

$$\triangle E = -\frac{8}{9}\frac{e^2}{2a_o} \tag{20}$$

which is equivalent to replacing ϵ_q by ϵ_3, the energy of the level with principal quantum number 3, in every term of (16). The first term of (18) falls off as $1/r^4$ and so Unsöld's approximation preservest he correct value for the dipole polarizability of the atom.

In order to perform the summation in expression (9) for f^{P}_{B2} we may make an analogous approximation to that proposed by Unsöld for summing (16). Thus we replace k_q by k_m in every term of (9). Then it may be readily shown, using (10) with $q = m$, that for $k_o\, a_o << 1$

$$f^{P}_{B2} \cong -\frac{1}{4\pi}\left(\frac{2M}{\hbar^2}\right)\int \exp ik_o\,(\hat{n}_o - \hat{n}).\, r\ \frac{1}{\epsilon_o - \epsilon_m}\ \underset{q \neq o}{S}\ V^{*}_{qo}\,(r)\ V_{qo}(r)\ dr. \tag{21}$$

The Massey and Mohr approximation replaces k_q by the wave number k_o of the incident particle. This is clearly a poor approximation since it is equivalent to putting $\Delta E = o$ in (17) which results in an infinite value for the polarizability of the atom. A more satisfactory approximation is to put $k_m = k_3$ where

$$\frac{\hbar^2}{2M}(k_3^2 - k_o^2) = \epsilon_o - \epsilon_3 \tag{22}$$

which ensures that the correct value for the dipole polarizability of the atom enters into the formulation.

With $k_q = k_3$ the evaluation of expression (9) for f^{P}_{B2} presents no difficulty since the method described by Dalitz (1951) may be employed. The distortion term $q = o$ of expression (8) for f_{B2} can be calculated separately as has been done by Kingston and Skinner (1961) for electron impact.

The case of excitation may be treated in an analogous fashion. However caution needs to be exercised in connection with the intermediate states which are degenerate with the final state. The most satisfactory procedure appears to be to consider these independently as has been done by Kingston, Moiseiwitsch and Skinner (1961) for the 1*s*-2*s* excitation of atomic hydrogen by electron and proton impact.

Finally there is a reservation regarding the applicability of the Unsöld type approximation to scattering problems which should be mentioned. It may be that f^{P}_{B2} is rather sensitive to the values of k_q employed in expression (9) even at high energies. If this should be the case the approximation suggested in the present paper will be unsatisfactory. In order to test the usefullness of this approximation, detailed calculations are to be performed.

ACKNOWLEDGMENT

It is a great pleasure to acknowledge the hospitality of Dr Charles J. Cook of Standford Research Institute where this work was carried out. It was supported

by National Aeronautics and Space Administration 1520 H St., N. U., Washington, 25, DC. Contract No. NASW-80.

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RECENT WORK ON PROBLEMS OF ELECTRON COLLISIONS WITH ATOMS AND IONS

By

M. J. SEATON

Department of Physics, University College, London, England

ABSTRACT

Recent ionization calculations show that inclusion of exchange gives improved agreement with experiment. Cross sections for ionization of highly ionized atoms may be estimated with good accuracy. The results obtained are used to calculate the ionization equilibrium in the solar corona and it is found that ionization theory gives coronal temperatures which are definitely lower than those obtained from line widths interpreted assuming thermal Doppler broadening.

Various formulae have been proposed for estimating cross sections for optically allowed transitions. It is shown that quite good results may be obtained. For exact resonance collisions, of the type $nl \rightarrow nl \pm 1$, the usual theory gives infinite cross sections but finite results are obtained on introducing suitable cut-offs at large impact parameters.

Calculations of recombination spectra have been made in two different ways: neglecting $nl \rightarrow nl \pm 1$ collisions, and assuming collisional $nl \rightarrow nl \pm 1$ transitions to be faster than radiative transitions. It is shown that, even for the low densities in gaseous nebulae, some allowance for $nl \rightarrow nl \pm 1$ collisions must be made.

1. IONIZATION OF ATOMS AND IONS BY ELECTRON IMPACT

It is not too difficult to give an exact formulation of the problem of electron collisions with atoms or ions when only elastic scattering, or excitation, can occur. With a nucleus of charge Z and N atomic electrons, the potential far from the atom is of the form* $V(r) = -z/r$, where $z = (Z - N)$. For neutral atoms, $z = 0$, the asymptotic forms of the wave function are expressed in terms of the functions

$$\frac{e^{\pm ikr}}{r} . \tag{1}$$

With $z \neq 0$, the corresponding Coulomb forms must be used,

$$\frac{e^{\pm i(kr + z/k \,.\, \ln r)}}{r} . \tag{2}$$

The formulation of ionization problems is more difficult, since one must consider screening effects with two outgoing electrons. Suppose that the initial ion, before ionization occurs, has N electrons and a charge $z = (Z - N)$. After ionization, let one of the outgoing electrons have velocity k and position r and let the other electron have velocity k' and position r'. Let $V = -\zeta/r$ be the effective potential, far from the ion, for the electron with velocity k. Assuming ζ not to depend on angles, Seaton (1962*a*) shows that

$$\zeta = \begin{cases} z & \text{for } k > k' \\ z + 1 - k/k' & \text{for } k < k' \end{cases} . \tag{3}$$

* We use atomic units throughout.

Thus the other electron gives complete screening if it is slower, incomplete screening if it is faster.

In a classical theory one would have

$$\frac{\zeta}{r} = \frac{(z+1)}{r} - \frac{1}{|r - r'|} . \tag{4}$$

Since both electrons may be considered to start out from the origin at the time $t = 0$, at time t one has

$$r = kt, \quad r' = k't \tag{5}$$

and therefore

$$\zeta = z + 1 - \frac{k}{|k - k'|} . \tag{6}$$

Using the expansion

$$\frac{1}{|k - k'|} = \begin{cases} \frac{1}{k} + \frac{k.k'}{k^3} + \ldots & \text{for } k > k' \\ \frac{1}{k'} + \frac{k.k'}{k^3} + \ldots & \text{for } k < k', \end{cases} \tag{7}$$

it is seen that one recovers (3) on taking only the spherically symmetric part of (6). However, the work of Peterkop (1960, 1961) indicates that (6) should be used in an exact formulation of the collision problem.

Special problems also arise in the treatment of electron exchange. In an elastic scattering, or excitation problem, one may first treat the two electron as though they were distinguishable. If the incident electron is scattered one has an amplitude f and if the incident electron is captured and the atomic electron ejected one has an amplitude g. Allowing for indistinguishability, and for the correct symmetry properties of the complete wave function, the cross section is determined by $|f \pm g|^2$. For electron-hydrogen scattering the cross section is proportional to

$$1/4 \; |f + g|^2 + 3/4 \; |f - g|^2 . \tag{8}$$

In an ionizing collision both electrons are ejected and this means that one has a simple relation between f and g. With a suitable choice of the phases used in defining f and g, Peterkop (1961) shows that

$$g(k, k') = f(k', k) \tag{9}$$

and therefore

$$f \pm g = f(k, k') \pm f(k', k) \tag{10}$$

The following methods may be used to calculate ionization cross sections:

(i) *The Coulomb-Born approximation.* One uses atomic continuum functions

for the ejected electron and Coulomb functions of charge z for the incident and scattered electron. For hydrogenic ions of charge $z = (Z - 1)$ one has

$$f_{CB}(k, k') =$$

$$-(2\pi)^{-5/2} \int \varphi(-k', z+1, r') \varphi(-k, z, r) \frac{1}{|r-r'|} \psi_0(r') \varphi(k_0, z, r) \, d^3r \, d^3r', \tag{11}$$

where ψ_0 is the bound state function of the ion and

$\varphi(k, z, r)$ is a Coulomb function with asymptotic form

$$\varphi(k, z, r) \sim e^{ik.r} [kr - k.r]^{-i\gamma} + e^{ikr} [kr - k r]^{i\gamma - 1} \frac{\gamma \Gamma(1 - i\gamma)}{\Gamma(1 + i\gamma)}, \tag{12}$$

where $\gamma = z/k$. For neutral atoms, $z = 0$, (11) reduces to the usual Born approximation.

(ii) *The Coulomb-Born-Oppenheimer approximation.* The exchange amplitude is calculated from

$$g_{CBO}(k, k') =$$

$$-(2\pi)^{-5/2} \int \varphi(-k', z+1, r) \varphi(-k, z, r') \left[-\frac{1}{r} + \frac{1}{|r-r'|} \right] \psi_0(r') \varphi(k_0, z, r) \, d^3r \, d^3r'. \tag{13}$$

The expressions (11) and (13) are used only for $k > k'$, so that the faster electron sees the smaller effective charge. The contribution from $k < k'$ is then obtained using (9).

(iii) *The Coulomb-Born-Exchange approximation.* The cross section is calculated using (10) and (11).

(iv) *Distorted Wave approximations.* One uses expressions similar to (11) and (13) with functions φ calculated in the Hartree fields of the initial and final ion.

Results are expressed in terms of the reduced cross section,

$$q = \left(\frac{I}{I_H} \right)^2 \frac{Q}{n\pi a_0^2} \tag{14}$$

where Q is the actual ionization cross section, n is the number of atomic electrons with ionization potential I, and I_H is the hydrogen ionization potential. If W is the kinetic energy of the incident electron, classical theory suggests that q, as a

function of (W/I), should be similar for different systems. The Born approximation gives q to be the same function of (W/I) for all ions in an iso-electronic sequence. Figure 1 gives some results for q against log (W/I). We draw the following conclusions:

(*i*) Inclusion of exchange gives smaller cross sections at low energies and improved agreement with experiment. The trend may be understood in terms of the exclusion principle. At low energies one has two slow electrons and the exclusion principle brings about a reduction in the cross section while at high impact energies the main contribution comes from states in which one electron is fast and the other is slow, and the exclusion principle is then of less importance.

(*ii*) For a fixed value of (W/I), similar result for q are obtained for different systems but, for small (W/I), there is some tendency for q to increase as z increases.

2. THE IONIZATION EQUILIBRIUM IN THE SOLAR CORONA

The ionization equilibrium depends on the processes

$$X^{+m} + e \rightarrow X^{+m+1} + e + e \qquad (15)$$

and

$$X^{+m+1} + e \rightarrow X^{+m} + h\nu \qquad (16)$$

The equilibrium, which depends only on temperature and not on density, has been calculated by Seaton (1962*b*) using reduced ionization cross sections consistent with the results of Figure 1. In Figure 2 we give results for log $[N(Fe\ X)/N(Fe)]$ as a function of temperature, $N(Fe\ X)$ being the number of $Fe\ X$ ions, (Fe^{+9}), and $N(Fe)$ the number of Fe atoms in all stages of ionization. It is seen that strong $Fe\ X$ emission is to be expected for $T \simeq 5 \times 10^5\ ^\circ K$. From the widths of the coronal $Fe\ X$ lines, interpreted assuming thermal Doppler broadening, Billings (1961) obtains temperatures of $1{\cdot}7 \times 10^6\ ^\circ K$. From the results of Figure 2 it seems most unlikely that there could be any appreciable $Fe\ X$ emission at a temperature as high as this and we are therefore led to question the thermal Doppler interpretation of the line widths. The discrepancy can be explained if one assumes the line widths to be affected by non-thermal motions. This explanation requires that about 1% of the total energy of the corona should be in the form of macroscopic motions.

Consideration of the ionization equilibrium for other ions suggests that the local temperature in the corona ranges from $5 \times 10^5\ ^\circ K$ in regions of strong $Fe\ X$ emission to $2 \times 10^6\ ^\circ K$ or more in regions of strong $Ca\ XV$ emission.

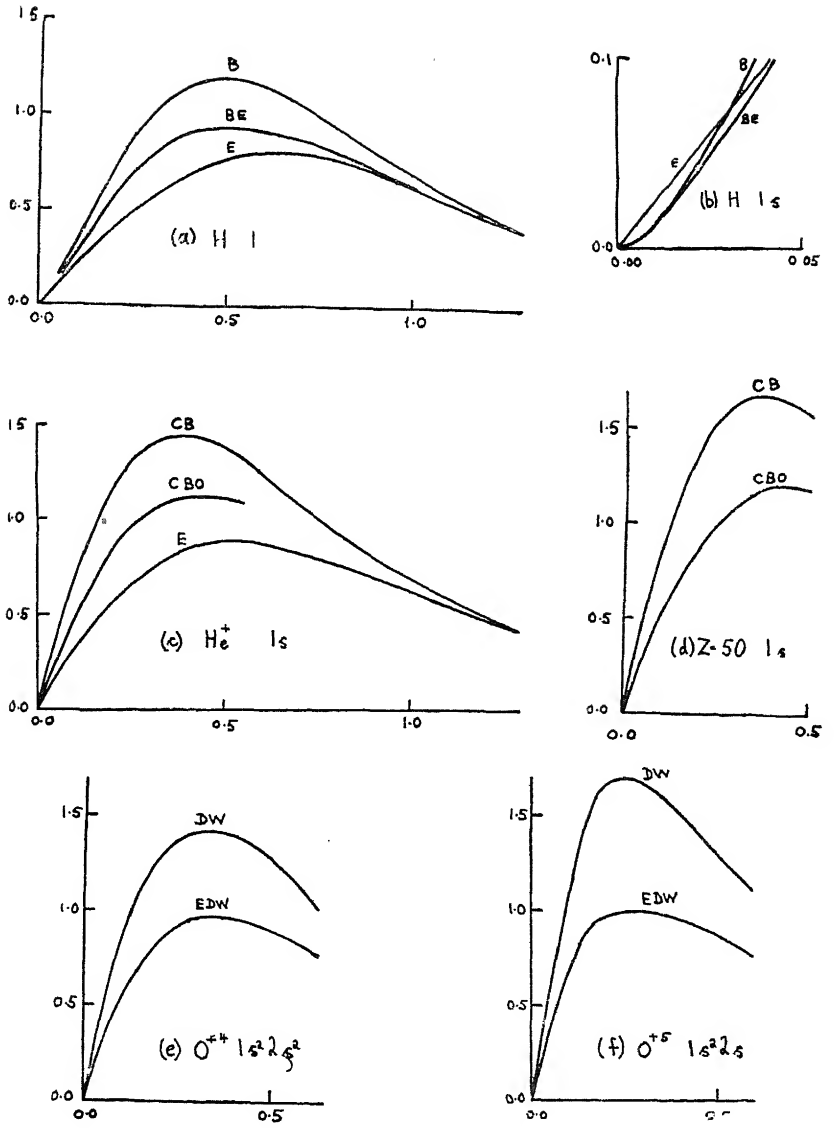

Fig. 1. Reduced ionization cross sections q (equation (14)), as functions of $\log_{10}(W/I)$. The following abbreviations are used: E, experimental results; B, Born approximations; BE, Born-Exchange approximation; CB and CBO, Coulomb-Born and Coulomb-Born-Oppenheimer approximations; DW and EDW, Distorted Wave and Exchange Distorted Wave approximations.

(a) *H*, 1*s*. Experimental results (Fite and Brackmann, 1958; Boksenberg, 1960; Rothes *et al.*, 1962), B and BE calculations, (Geltman, Rudge and Seaton, 1962).

(b) *H* 1*s* near threshold. Due to incorrect treatment of screening, the theoretical result give a wrong threshold law.

(c) He^+, 1*s*. Experimental results (Dolder, Harrison and Thonemann, 1961), CB and CBO calculations (Rudge and Burgess, 1962).

(d) Hydrogenic ion, $Z = 50$, 1*s*. *CB* and *CBO* calculations (Rudge and Burgess, 1962).

(e) and (f) O^{+4}, $1s^2\,2s^2$ and O^{+5}, $1s^2\,2s$. DW and EDW calculations (Malik and Trefftz, 1961, and Trefftz, 1962).

3. CROSS SECTIONS FOR OPTICALLY ALLOWED TRANSITIONS

Considerable effort has been devoted to the problem of obtaining quick yet reliable estimates of atomic collision cross sections. The best results are obtained for optically allowed transitions, for which the cross sections are often large and are of particular importance in various applications.

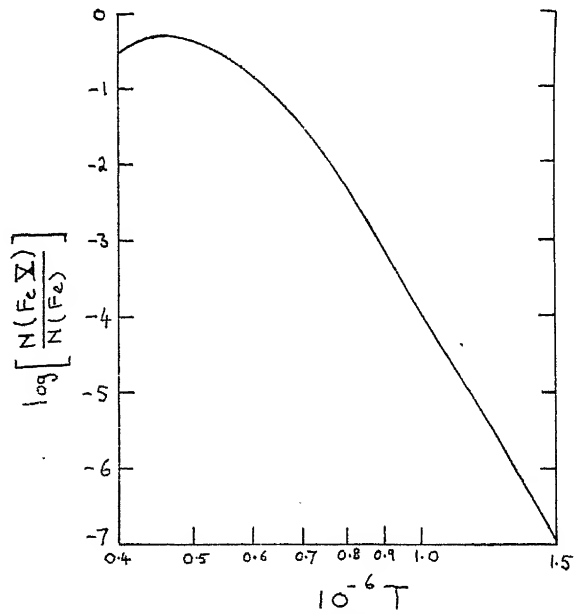

Fig. 2 The ionization equilibrium for *Fe X* in the solar corona.

With the colliding electron at the position r, the coupling between the atomic states i and j is determined by the interaction potential

$$V_{ji}(r) = \int \psi_j^* (r) \frac{1}{|r - r'|} \psi_i (r') d^3 r'. \tag{17}$$

Let r_a be comparable with the atomic radius and suppose r to be greater than r_a. Then

$$V_{ji}(r) \simeq \frac{r.(j \mid r' \mid i)}{r^3}, \tag{18}$$

where the dipole moment, $(j \mid r' \mid i)$, is non-zero for optically allowed transitions. This suggests that cross sections may be expressed in terms of the oscillator strength, f_{ji}, which is proportional to $|(j \mid r' \mid i)|^2$.

The following formula has been discussed by van Regemorter (1960, 1962), Burgess (1961) and Seaton (1962*a*):

$$Q(i \to j) = \frac{8\pi}{\sqrt{3}} \cdot \frac{I_H^2}{W_i \triangle E} \cdot f_{ji} \bar{g}(W_i / \triangle E) \pi \alpha_o^2, \tag{19}$$

where $\triangle E$ is the energy difference and W_i the energy of the electron incident on state i. Figure 3 shows the adopted curve for the function $\bar{g}$, obtained from experimental results for neutral atoms and from calculations for positive ions. The use of this approximation should give cross section estimates which are sufficiently accurate for many astrophysical applications but it will become less reliable for transitions, such as those between highly excited states, which are very different from those used to determine the function $\bar{g}$ of Figure 3.

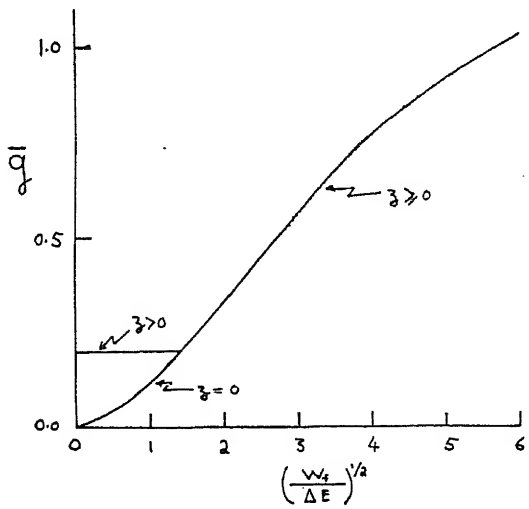

Fig. 3. The function $\bar{g}$ (equation (19)) against $(W_t/\triangle E)^{1/2}$, W_t being the electron kinetic energy when the atom is in the more highly excited of the two states involved in the transition. The low energy results for $z = 0$ and $z > 0$ are different due to different threshold laws for neutral atom and positive ion excitation.

Seaton (1962*c*) had made some improvements in the semi-classical impact parameter method. When a reciprocity condition is imposed, the semi-classical theory is found to give results in good agreement with quantal calculations. In using a potential of the form (18) it is necessary to introduce a cut-off for small impact parameters, at $R_0 \simeq r_a$. In the way in which this cut-off is determined,

the semi-classical theory is superior to the quantum mechanical Bethe approximation. Figure 4 shows that the impact parameter theory gives good agreement

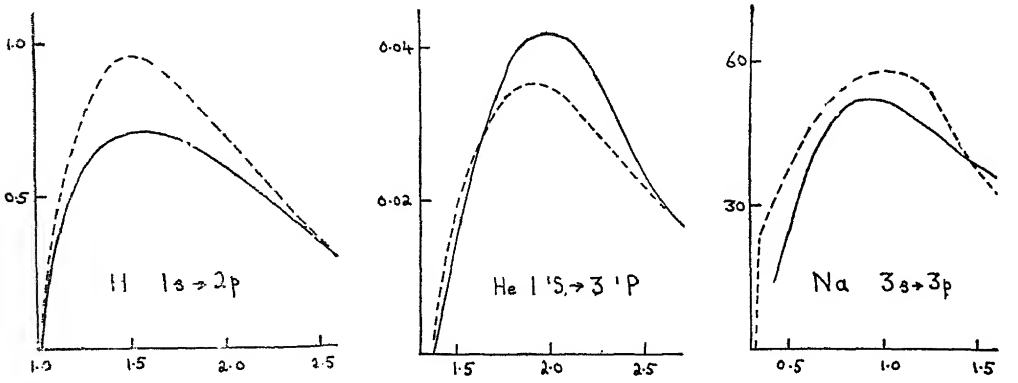

Fig. 4. Comparison of experimental cross sections (full line curves) and cross sections calculated by the impact parameter method (Seaton, 1962*c*). The cross sections are in units of πa_0^2 and the energy scale is $\log_{10} W$ where W is the electron kinetic energy in eV.

with three experimental results, in which the sizes of the cross section range over 3 orders of magnitude. The formulae are not quite so simple as (19) but have the advantage of being more accurate and of having a wider range of applicability.

4. EXACT RESONANCE COLLISIONS

In the impact parameter theory,

$$Q = \int_0^\infty P(R)\, 2\pi\, R dR \tag{20}$$

where $P(R)$ is the transition probability for orbits of impact parameter R. Using (18) one obtains, for $\Delta E = 0$,

$$P(R) = \frac{4}{3}\,\frac{I_H}{W}\,\frac{|(i|r|j)|^2}{R^2}. \tag{21}$$

Substitution in (20) gives an integral which diverges at both $R = 0$ and $R = \infty$. We therefore consider

$$Q = \int_{R_1}^{R_2} P(R)\, 2\pi\, R dR$$

$$= \frac{8\pi}{3}\left(\frac{I_H}{W}\right) |(i|r|j)|^2 \ln(R_2/R_1) \tag{22}$$

The conservation condition is $P(R) \leqslant 1$. The lower limit, R_1 in (22), may be determined by the relation $P(R_1) = \frac{1}{2}$. If this gives R_1 to be less than the atomic radius, r_a, we put $R_1 = r_a$.

The time duration of the collision is of order $T_c = kR$ where, in atomic units, $W = \frac{1}{2}k^2$. The collision will not produce a transition if this is large compared with the radiative lifetime, τ. The upper limit is taken to be $R_2 = \tau/k$ giving

$$Q = \frac{8\pi}{3} \cdot \left(\frac{I_H}{W} \right) \mid (i \mid r \mid j) \mid^2 ln\,(\tau/k\,R_1). \tag{23}$$

Pengelly and Seaton (1963) show that this is a good approximation if $ln\,(\tau/k\,R_1) >> 1$. The formula is equivalent to that obtained assuming inexact resonance and then taking the energy difference, $\triangle E$, to be equal to the radiation damping width, $\triangle E \sim \tau^{-1}$ atomic units.

The results are of interest for the calculation of cross sections for $nl \rightarrow nl \pm 1$ transitions between excited states of hydrogen. The values of R_2 turn out to be vary large. In a plasma the effective range of the potentials is equal to the Debye radius, R_D. If (τ/k) is larger than R_D one should take $R_2 = R_D$.

5. CALCULATIONS OF RECOMBINATION SPECTRA

Recombination spectra are important in gaseous nebulae. The problem is to calculate the intensity of the spectrum resulting from recombination and cascade,

$$\begin{aligned} &H^+ + e \rightarrow H\,(nl) + h\nu, \\ &H\,(nl) \rightarrow H\,(n'\,l') + h\nu_{nn'}\,. \end{aligned} \tag{24}$$

The total number of quanta emitted in the $n \rightarrow n'$ line, per cm^3 per sec, is $N(e)\,N(H^+)\,\alpha_{nn'}\,(T)$ where $\alpha_{nn'}$ is the effective recombination coefficient for the line. Calculations have been made in two ways:

(*a*) It is assumed that collisional $nl \rightarrow nl \pm 1$ transitions are faster than radiative transitions. One then has

$$N_{nl} = \frac{(2l+1)}{n^2}\,N_n \tag{25}$$

where N_{nl} is the number of H atoms in the state nl.

(*b*) It is assumed that collisional $nl \rightarrow nl \pm 1$ transitions may be neglected, so that the whole problem is determined by the processes (24).

Solutions assuming (25), and taking account of an infinite number of levels n, have been obtained by Baker and Menzel (1938) and, more accurately, by Seaton (1959). Burgess (1958) has obtained solutions using method (*b*) for $n \leqslant 12$ and method (*a*) for $n > 12$. More recently, Pengelly (1962) has obtained solutions for method (*b*) and an infinite number of levels. For some lines it turns out that there are quite considerable differences between the results obtained by the two methods. This is illustrated in Table 1, which gives values of the effective recombination

TABLE 1

The effective recombination coefficient, $\alpha_{4,3}$ (units $cm^5\ sec^{-1}$), for the He II line, λ 4686. Calculations for nebulae optically thick in He II Lyman lines.

$10^{-4} \times T$		1	2	4	8
$10^{14} \times \alpha_{4,3}$	(a)	20·8	11·8	6·4	3·3
	(b)	37·2	17·8	8·2	3·6

coefficient for the strong He II line at λ 4686. There are also considerable differences in the relative intensities. The relative intensities observed in gaseous nebulae, in the spectra of *H I* and of He II, agree fairly well with those calculated for case (*a*) and disagree with those for case (*b*). This at first seemed rather surprising, since at the low densities in nebulee ($N(e) \simeq 10^4\ cm^{-3}$) it was not expected that collisional processes would compete with radiative processes. A more detailed study has shown that the main differences between the results obtained by the two methods are determined by the assumptions made for the very high states, $n \simeq 20$ or more. Using the theory of exact resonance collisions discussed in section 4 above, it is found that collisional $nl \rightarrow nl \pm 1$ processes are in fact faster than radiative processes for $n \geqslant 20$. When these are taken into account, one obtains satisfactory agreement with observations.

ACKNOWLEDGEMENTS

I am indebted to Mr. M. Rudge, Dr. A. Burgess, Dr. E. Trefftz and Mr. M. Pengelly for permission to quote their work in advance of publication.

Some of the work discussed was supported by the Atomic Energy Research Establishment and I acknowledge with thanks their permission to publish.

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ON THE CONNECTION BETWEEN THE THEORIES OF COLLISIONS AND OF ATOMIC SPECTRA

By

U. FANO *and* F. PRATS

National Bureau of Standards, Washington, D. C., U. S. A.

ABSTRACT

The Slater method for calculating discrete energy eigenstates of atoms as superpositions of states of the independent particle approximation is extended to the continuous spectrum. The Schrödinger equation reduces to the inhomogeneous equation for a reaction matrix which appears suitable for direct numerical solution. A separate algebraic eigenvalue problem must be solved to calculate eigenfunctions with specified behavior at infinity, including those which diagonalize the scattering matrix.

An electron colliding with a neutral atom constitutes a system that may be regarded as a negative ion in an unbound state. This point of view may be applied in general to collisions of a particle with an n-particle system by treating all $n+1$ particles on a par, instead of singling out the incident particle. This approach should be particularly suitable for low energy collisions in which the incident particle interacts rather closely with one or more of the other particles. Such a treatment would constitute an extension of the theory of bound states which, starting from the independent particle approximation, has rather successfully handled even atoms with many external electrons.

With these thoughts in mind a formalism has been developed that describes the unbound states of atoms, molecules or nuclei—*i.e.* states with energy in excess of the requirement for dissociation—and relates on the one hand to the formal theory of scattering and on the other to the theory of bound states of atoms. The unbound states can arise either through combination of an incident particle and of a preexisting bound system, or from bound states through energy absorption from light or other external agent. While applications of this formalism to realistic calculations of atoms are being planned, an outline of its principles and basic formulas is presented in this paper.

Let us consider first the relevant aspects of the theory of bound states of atoms. This theory starts ordinarily from the approximation of independent electrons in a central field, in which an atomic state is initially classified by quantum numbers that identify the states of individual electrons (*i e.* the configuration of the atom) and possibly the coupling of their angular momenta. The actual interaction among electrons has then the effect of mixing different states of the initial approximation (u_m, u_n, . . .) into new states

$$\psi = \Sigma_m a_m u_m \qquad (1)$$

The coefficients a_m are often obtained adequately by perturbation procedures or by diagonalizing numerically matrices of manageable size. This procedure,

which we shall call the "Slater approach", has been applied mainly to the ground state and to the lower excited states, presumably because of their greater interest. Extension to higher excited states and to the continuum requires one to consider an increasing number of initial states and the fact that the separation of their energy levels decreases. However, favorable circumstances will be seen to compensate at least some of these difficulties.

The usual perturbation procedure is an expansion in powers of the ratio of the off-diagonal Hamiltonian matrix element V_{mn}, which pertains to any pair of first approximation states, to the energy difference of these states, $E_m - E_n$. With increasing excitation one meets values of $E_m - E_n$ that approach zero, but the corresponding V_{mn} also approaches zero. Applicability of the perturbation procedure depends on the limit of the ratio $V_{mn}/(E_m - E_n)$, which is generally finite and presumably much smaller than one. As one would surmise, this limit will appear in the perturbation theory of continuous spectra and is simply the *matrix element* itself, $V_{E',E}$, between continuum states of energies E' and E *normalized per unit energy range*. This matrix element has the dimensions of a pure *number*; it might be regarded as the product of the strength of the interaction and of the duration of a collision, divided by $\hbar$.

In essence, the Slater approach to the study of bound states represents the Schrödinger equation in the scheme of the first approximation states u_m, where it takes the form of an algebraic system

$$E_m a_m + \Sigma_n V_{mn} a_n = E a_m, \tag{2}$$

with the eigenvalue E and eigenvector $(a_m, a_n \ldots)$, which is amenable to approximate numerical solution. Extension to unbound states causes the $\Sigma_n V_{mn} a_n$ to be replaced by an integral over energy and causes the solution of the system to become sigular in that the analog of the coefficient $E - E_m$ vanishes for some of the eigenvector components. This singularity can, however, be treated analytically[1]. The integrals can be reduced adequately to algebraic sums of manageable length if their integrands are sufficiently smooth functions of the energy. The present development relies on the surmise that this reduction will often be successful.

Specifically, we shall consider a system of n atomic electrons $1, \ldots, r, \ldots, s, \ldots n$, with the Hamiltonian

$$H = \Sigma_r (T_r + U_r) + \tfrac{1}{2} \Sigma_{r \neq s} V_{rs}, \tag{3}$$

where T_r is the kinetic energy of the r-th particle, U_r its potential energy in the nuclear field and V_{rs} the interaction energy of r and s. An additional central potential V_r will be added and subtracted for each particle, to yield

$$H = \Sigma_r (T_r + U_r + V_r) + \tfrac{1}{2} \Sigma_{r \neq s} \left[V_{rs} - \frac{1}{n-1} (V_r + V \right] =$$

$$= \Sigma_r (T_r + \bar{U}_r) + \tfrac{1}{2} \Sigma_{r \neq s} \bar{V}_{rs} = H_0 + \bar{V} \tag{4}$$

where $\bar{U}_r = U_r + V_r$, $H_0 = \Sigma_r (T_r + \bar{U}_r)$ and where V_r should be chosen so as to reduce the magnitude of the residual interaction $\bar{V}$. Following the Slater approach, we shall assume that eigenfunctions of $T_r + \bar{U}_r$ have been obtained—in general, by numerical integration—[2] and that the effect of $\bar{V}$ remains to be studied. Eigen-

states of H_0, constructed as antisymmetrized products of eigenfunctions of $T_r+\bar{U}_r$ (or as linear combinations of such products with the same energy) will be indicated by $u_{i\varepsilon}$. Here ε represents the eigenvalue of H_0 corresponding to $u_{i\varepsilon}$ and belongs generally, but not necessarily, to a continuous spectrum, and i indicates the additional group of discrete numbers that are required to identify $u_{i\varepsilon}$[3]. An eigenstate of the complete Hamiltonian is then represented, in analogy to (1), by

$$\psi=\Sigma_i \int d\varepsilon\, a_{i\varepsilon}\, u_{i\varepsilon} \tag{5}$$

The Schrödinger equation analogous to (2) is

$$\varepsilon a_{i\varepsilon}+\int d\varepsilon'\, \bar{V}_{i\varepsilon,\, j\varepsilon'}\, a_{j\varepsilon'}=E\, a_{i\varepsilon} \tag{6}$$

where $\bar{V}_{i\varepsilon,\, j\varepsilon'}$ is the matrix element of the residual interaction $\bar{V}$ between the states $u_{i\varepsilon}$ and $u_{j\varepsilon'}$.

Before discussing our suggested method for solving (6), let us summarize the approach to unbound states from scattering theory. One considers an initial state with one particle, say the n - th one, in a free state (*i.e.* in an eigenstate of T_n) and the remaining particles in a bound state. Thereby one decomposes in effect the Hamiltonian (4) in the form

$$H=T_n+H^{(n-1)}+\bar{U}_n+\sum_{r=1}^{n-1}\bar{V}_{nr} \tag{7}$$

and treats $\bar{U}_n+\Sigma_{r=1}^{n-1}\bar{V}_{nr}$ as a perturbing interaction. (A different form of H must be considered in connection with the final state in the case of a rearrangement collision.) Useful formal solutions of the Schrödinger equation are considered[4], in terms of which one may express properties of unbound states even when little is known about the particle interactions or about the bound states of $H^{(n-1)}$. For example, if state of energy E is represented by an eigenstate ϕ_i of $T_n+H^{(n-1)}$ when the incident particle n is far from the others, its formal eigenstate including all outgoing scattered waves is

$$\psi^{(+)}=\phi_i+\frac{1}{E-H+i\eta}(\bar{U}_n+\Sigma_r \bar{V}_{nr})\,\phi_i\ , \tag{8}$$

where the limit $\eta\to 0$ is implied. Similarly, a state identified by its "final" form ϕ_f, in which particle n has separated from the others, is represented by the formal solution

$$\psi_f^{(-)}=\phi_f+\frac{1}{E-H-i\eta}\left(\bar{U}_n+\Sigma_r \bar{V}_{nr}\right)\phi_f, \tag{8'}$$

which includes different incoming waves.

Characteristics of the formal solutions are the unitary scattering matrix S and the related hermitian reaction matrix K. The matrix element of S for scattering from ϕ_i into ϕ_f is

$$S_{fi} = \left(\frac{1+i\pi K}{1-i\pi K}\right)_{fi} = \left(\psi_f^{(-)}, \psi_i^{(+)}\right). \tag{9}$$

In general the K matrix obeys the inhomogeneous operator equation

$$K = V' + PV' \frac{1}{E-H'} K \ , \tag{10}$$

where P indicates "principal part" of any integration over the singularity at $H' = E$, where V' is the portion of H disregarded in the initial approximation and where $H' = H - V'$.

Many approximations to the solution of the Schrödinger equation for scattering problems have been sought in cases where sufficient information is available on the forces. Variational methods have been used, as well as approximate reduction of the complete equation to an integro-differential system in the space variables.[5] Keeping the size of this system manageable has necessitated rather unrealistic approximations.[6] Attention has also been given[7] to the problem of minimizing $\Sigma_r \bar{V}_{nr}$ in (7) by suitable choice of V_r, so that this term might be disregarded altogether and eigenstates of $T_n + \bar{U}_n$ would constitute an adequate approximation to the scattering of a single particle.

From the standpoint of scattering theory, our study of unbound states of a system by the Slater approach looks as follows. Initial use of unbound eigenstates of H_o, which reflect the influence of the central protential $\Sigma_r \bar{U}_r$, constitutes advance knowledge of a factor S_o of the scattering matrix. This factor is expressed in terms of the phase shifts δ_{0i} in the asymptotic representation of the initial wave functions u_{iE} at large distance from the atom. The complete scattering matrix can thus be factored out in the operator form

$$S = S_o^{\frac{1}{2}} \bar{S} S_o^{\frac{1}{2}} \tag{11}$$

or, in the u_{iE} representation,

$$S_{ij} = e^{i\delta_{oi}} \bar{S}_{ij} e^{i\delta_{oj}} \ , \tag{11'}$$

where $\bar{S}$ is a reduced scattering matrix, which represents the effect of the residual interaction $\bar{V}$[8]. To the reduced $\bar{S}$ pertains a reduced reaction matrix $\bar{K}$ related to it by the usual formula

$$\bar{S} = \frac{1+i\pi\bar{K}}{1-i\pi\bar{K}} \tag{12}$$

After all these preliminaries we return now to the Schrödinger equation (6) and perform on it the change of dependent variable

$$a_{i\varepsilon} = P\frac{1}{E-\varepsilon}A_{i\varepsilon} + \delta(\varepsilon - E)\ B_i \tag{13}$$

In this formula P indicates that the Cauchy principal part should be taken in any integration over ε, $A_{i\varepsilon}$ is the new dependent variable, $\delta(\varepsilon - E)$ is the Dirac function and B_i an integration constant. This change of variable is designed[1] so that the product $(E-\varepsilon)\,a_{i\varepsilon}$ in (6) reduces to $A_{i\varepsilon}$ and is independent of B_i, since $x\,\delta(x) = 0$.

Substitution of (13) into (6) yields

$$A_{i\varepsilon} = \Sigma_j P\int d\varepsilon'\,\bar{V}_{i\varepsilon,j\varepsilon'}\frac{1}{E-\varepsilon'}A_{j\varepsilon'} + \Sigma_j\,\bar{V}_{i\varepsilon,jE}\,B_j . \tag{14}$$

This equation is linear and inhomogeneous and determines the $A_{i\varepsilon}$ as linear functions of the integration constants B_j. Accordingly we write

$$A_{i\varepsilon} = \Sigma_j\,\bar{K}_{ij}(\varepsilon)\,B_j , \tag{15}$$

and substitute this expression into (14). The result has the form of a linear homogeneous algebraic system in the B_j, which is fulfilled by arbitrary B_j only if the coefficient of each B_j vanishes. This requirement yields for $\bar{K}_{ij}$ the inhomogeneous equation

$$\bar{K}_{ij}(\varepsilon) = \bar{V}_{i\varepsilon,jE} + \Sigma_l\ P\int d\varepsilon'\ \bar{V}_{i\varepsilon,l\varepsilon'}\frac{1}{E-\varepsilon'}\ \bar{K}_{lj}(\varepsilon') . \tag{16}$$

Eq. (16) is just the representation of the operator equation (10) in the base of the initial states and thus identifies $\bar{K}_{ij}(\varepsilon)$ as an element of the reduced reaction matrix.[9]

The Schrödinger equation for unbound states has thus been reduced to an inhomogeneous integral form. (An eigenvalue problem will, however, appear below in the discussion of the constants B_i). It is a main point of this paper that Eq (16) is particularly favorable for numerical solution. The remaining singularity in the integral should cause no serious difficulty because the integration over its principal part gives a finite result. This singularity can also be pushed further aside as will be explained elsewhere.

The matrix elements $\bar{V}_{i\varepsilon,j\varepsilon'}$ of the reduced interaction normalized per unit energy range appear clearly in Eq. (16) in the role of perturbation parameters. Whenever all these matrix elements are much smaller than one, Eq. (16) is

readily solved by iteration, *i.e.* by expressing $\bar{K}_{ij}(\varepsilon)$ as a Neuman series. In fact, the first approximation solution

$$\bar{K}_{ij}(\varepsilon) \simeq \bar{V}_{i\varepsilon,jE} \tag{17}$$

might often be adequate[10]. More generally it may happen that only the matrix elements of $\bar{V}$ in a limited range of $i\varepsilon$ have sizeable values. The values of $\bar{K}$ in this range would then be obtained by more accurate numerical procedures, whereas the remaining values would be given adequately by (17). In any event, an exploratory numerical mapping of the whole matrix $\bar{V}$ appears to be essential to determine which effects of configuration mixing are important and require a special treatment.

It is important for the expeditious numerical solution of (16) that $\bar{V}_{i\varepsilon,j\varepsilon'}$ be a smooth function of ε and ε'. Any departure from smooth, almost monotonic, trend of this function would indicate the occurence of some physical circumstance that requires special treatment. For example a sharp peak would probably indicate resonance with a discrete state that has not been properly singled out in the choice of the initial set of first approximation states $u_{i\varepsilon}$. A modification of this set might then smooth out the peak. Any more specific discussion of this point should, however, be delayed until experience has been gathered on the actual solution of particular problems.

Let us consider now the determination of the integration constants B_j to fit whatever physical conditions identify a specific unbound state with a given energy E. To begin with, the B_j will be normalized so that the wave function (5) is normalized per unit energy range. To this end one can substitute (15) into (13) and then (13) into (5) and proceed in analogy to I, Eq. (9′) – (12). One finds the normalization condition

$$\Sigma_{ij}\, B_i \left[\pi^2 \Sigma_l\, \bar{K}_l\ (E)\, \bar{K}_{lj}(E) + \delta_{ij} \right] B_j = 1, \tag{18}$$

which, if the B_j are considered as components of a vector, reads

$$\tilde{B} \left[\pi^2\, \bar{K}^2 + 1 \right] B = 1 \tag{19}$$

Of special interest are the sets of constants $B^{(\mu)}_j$ which are eigenvectors of the matrix $\bar{K}_{ij}(E)$, such that

$$\Sigma_j\, \bar{K}_{ij}(E)\ \ B^{(\mu)}_j = \bar{k}_\mu\, B^{(\mu)}_i, \tag{20}$$

and which form an orthonormal system

$$\Sigma_i\, B^{(\nu)}_j \left(1 + \pi^2 \bar{k}^{\,2}_\mu \right) B^{(\mu)}_i = \delta_{\mu\nu} \tag{21}$$

The B_j are related to the phase shifts induced by the residual interaction. To bring out this relation, consider the asymptotic behaviour of the initial wave function $u_{i\varepsilon}$ when one particle is at a large distance r from the atom.

$$u_{i\varepsilon} \sim c_i \sin \left[k(\varepsilon) r - l_i \pi/2 + \delta_{oi} \right] / r \tag{22}$$

where c_i represents all factors irrelevant to us. Enter this expression in (5) with the coefficients $a_{i\varepsilon}$ from (13) and (15). It is then found, in accordance with I Eq. (5), that

$$\psi = \Sigma_i c_i \{ -\pi \cos [k(E) r - l_i \pi/2 + \delta_{oi}] \Sigma_j \overline{K}_{ij}(E) B_j + \sin [k(E) r - l_i \pi/2 + \delta_{oi}] B_i \}/r$$

$$= \Sigma_i c_i B_i \sin [k(E) r - l_i \pi/2 + \delta_{oi} + \delta_i]/r \cos \delta_i , \tag{23}$$

where the phase shift δ_i is defined by the equation

$$\pi \Sigma_j \overline{K}_{ij}(E) B_j = -\tan \delta_i B_i \tag{24}$$

In particular, if $B_i = B^{(\mu)}{}_i$ according to (20),

$$\tan \delta^{(\mu)}{}_i = -\pi \overline{k}_\mu \tag{25}$$

independently of i. (In fact (24), which defines δ_i, includes (20) as the special case where δ_i is independent of i.) In general, (24) establishes a relationship between the sets of parameters δ_i and B_i. When physical conditions determine one of these sets, (24) determines the other.

The most familiar situation in scattering theory is that in which the state involves one particle incident in "channel" i and a superposition of outgoing particles in other channels. This situation is represented by the well known set of phase shifts

$$\delta_j = i\infty \quad or \quad \tan \delta_j = -i \quad for\ j \neq i , \tag{26}$$

the remaining phase shift δ_i being determined by the condition that the system (24) has non-vanishing solutions B_j .

Another important situation is that in which the scattering matrix S is diagonal and the state is represented by a superposition of standing-wave functions with total phase shifts $\delta_{oi} + \delta_i = \delta$ independent of i. This state is identified mathematically by entering $\delta_i = \delta - \delta_{oi}$ in (20) and solving this system so as to determine the eigenvalues δ and eigenvectors B_i of the system

$$\Sigma_j K_{ij}(E) B_j = -\pi^{-1} \tan (\delta - \delta_{oi}) B_i \tag{27}$$

(The δ_{oi} are, of course, known characteristics of the initial wave functions u_{iE})

The eigenvalue problem (27) which determines the phase shifts δ relates closely to the eigenvalue problem which determines the energy levels in the discrete spectrum. For example when high energy levels of a neutral atom are expressed by the Rydberg formula $E_n = -13{\cdot}6/(n-\sigma)^2$ ev, the quantum defect σ multiplied by π equals the excess of the phase shift δ of the adjoining unbound states over the corresponding phase shift for unbound states of the H atom. This connection, which has been utilized in I, App. B, is straightforward in simple cases, but will require additional study in the presence of complex configuration interactions.

In this connection, it may be worth discussing somewhat further the separation of the treatment of unbound states into two steps represented respectively by (16) and (27). Eq. (16) utilizes the full matrix $\bar{V}_{i\varepsilon,j\varepsilon'}$ as input and yields the matrix $\bar{K}_{ij}(E)$ on the energy shell, which serves in turn as input to the eigenvalue equation (27). One might say that (16) serves to calculate the contribution to ψ of states off the energy shell in terms of the contribution of the states on the energy shell. The matrix $\bar{K}_{ij}(E)$ takes into account implicitly the admixture of states off the energy shell, as shown by setting $\varepsilon = E$ in (16), and in essence replaces the direct interaction $\bar{V}_{iE,jE}$ between u_{iE} and u_{jE} with an effective interaction. This effective interaction determines the mixing of degenerate states on the energy shell through the eigenvalue equation.

One might conceive of trying the same approach in the treatment of bound states. To this end, the equations (2) might be separated into two groups, one of which consists of the equations with values of E_m degenerate, or quasi-degenerate, and close to an eigenvalue E of interest. The remaining equations would then be utilized to eliminate the a_m pertaining to states that are not quasi-degenerate. The eventual eigenvalue problem would then involve only the limited set of states of the first group. This procedure is not straightforward, however, in that the elimination of the second group of a_m implies advance knowledge of E, which is fixed in advance for unbound states but is unknown for bound states. One would, then, have to start the procedure with an estimated E.

This difficulty is not serious for weakly bound states, whose energy levels form a dense spectrum. For this reason one may expect that the procedure developed for unbound states can be extended to weakly bound states. (This procedure has, of course, the advantage that whole groups of states $u_{i\varepsilon}$, whose values of ε fill a sizeable energy band, are treated as single units.) Application to tightly bound states would be more difficult, but it should be noted that direct numerical solution of the complete system (2) has actually never been attempted. One usually truncates this system by considering only a limited set of states m and disregarding the matrix elements that link these states to states n of substantially different energy.

In fact, the procedure that is usually followed in the theory of low atomic energy levels bears an interesting relationship to the use of a reaction matrix. The matrix elements $\bar{V}_{mn}$ are not actually calculated by integrating over all variables of the wave functions; only the angular integrations are carried out, but the radial integrals ("Slater integrals") are treated as free parameters, to be adjusted to best fit of the calculated eigenvalues to the experimental energy levels. This adjustment is understood to take into account implicitly some of the effect of mixing-in energetically distant configurations. One might describe this procedure as the replacement of the submatrix V_{mn} for a limited set of states by a matrix K_{mn} analogous to a reaction matrix. The dependence of this K_{mn} on the angular quantum numbers is bound to be the same as for V_{mn}, the dependence on radial quantum number is estimated by fitting to experimental data.

We may indicate now the connection between the present approach and the Brueckner method for the nuclear many-body problem.[11] Both methods may be said to involve the replacement of the residual interaction matrix $\bar{V}_{i\varepsilon,\, j\varepsilon'}$ with the reaction matrix $\bar{K}_{ij}(\varepsilon, \varepsilon')$, so that $\bar{K}$ represents an "effective interaction." (Indeed, substitution of (15) into (13) yield for $a_{i\varepsilon}$ a formula similar to a first order perturbation formula with the effective interaction $\bar{K}$.) However, the Brueckner method focusses on the initial determination of an effective two-particle interaction by a self-consistency requirement. In the present approach, self-consistency is utilized by implication only for the choice of the initial single particle potential $\bar{U}_r$ and no advance prescription is suggested for the solution of the reaction matrix equation (16). Our reaction matrix represents, in general, a many-particle interaction in that the "channels" i and j may differ by the quantum numbers of more than two particles.

Finally it may be noted that points of view related to those presented here are being put forth by different authors, in particular by Löwdin.[12] These approaches provide a quite general frame whose usefulness remains to be gauged by specific applications.

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2. Whereas in the Hartree method the potentials V_r are chosen to optimize the approximation of a single initial state $u_{i\varepsilon}$ which is of particular interest, it is the essence of our approach that a single V_r be chosen for the *whole set* $u_{i\varepsilon}$, to optimize the average approximation of a broad class of u_i. We aim at a flexible treatment that affords a reasonable, uniform approximation to a variety of parameters, including for example line strengths, rather than maximum accuracy of a single energy eigenvalue or phase shift.
3. When s is sufficiently large to permit double or multiple ionization, the distribution of this

energy among different particles is understood to be characterized by a parameter included in the index i. No serious difficulty is expected from this additional variable.

4. B. A. Lippman and J. Schwinger, *Phys. Rev.*, **79**, 46 (1950).

5. *See, e.g.*, H. S. W. Massey, *Encyclopedia of Physics, Springer, Berlin* (1956), vol. 36/2 pp. 285 ff.

6. The present paper emphasizes the direct solution of integral systems rather than of differential ones. We also take the first approximation energy ε as the main independent variable rather than a radial coordinate, because the $a_{i\varepsilon}$ are expected not to be oscillatory functions of ε.

7. M. H Mittleman and K. M. Watson, *Phys. Rev.*, 113, 198 (1959).

8. Formulas analogous to (11') are encountered in nuclear reaction theory.

9. $\bar{K}_{ij}(\varepsilon) = (u_{i\varepsilon} \mid \bar{K} \mid u_{jE})$ can be indicated as $\bar{K}_{i\varepsilon, jE}$ in full matrix notation and in accordance with the notation $\bar{V}_{i\varepsilon, jE}$ in (16). The elements of $\bar{K}$ diagonal in energy, *i.e.* the elements $\bar{K}_{iE, jE} = \bar{K}_{ij}(E)$ are those which are related to the scattering matrix $\bar{S}$ by (12); the scattering matrix is defined "on the energy shell" only, whereas the reaction matrix is also a matrix in the energy variable.

10. This first approximation solution is analogous to the "distorted wave Born" approximations.

11. See, *e.g.*, H. A. Bethe, *Phys. Rev.*, **103**, 1353 (1956).

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INELASTIC COLLISION OF IONS IN GASES

By

S. B. KARMOHAPATRO

Saha Institute of Nuclear Physics, Calcutta-9

INTRODUCTION

Studies on the inelastic collision of ions in gases are important, since such processes are involved in the problems of accelerators, high intensity mass spectrometers, thermonuclear reactors and ionospheric researches.

An energetic ion, in the energy range below the threshold of any nuclear reactions, by inelastic collision with gas atoms or molecules may produce some atomic reactions, which are not so prominent in the higher energy range.

Some of them are the following :

$$A^+ + B \rightarrow A + B^+ \quad (1)$$

$$A^+ + B \rightarrow A^+ + B^+ + e \quad (2)$$

$$A^* + B \rightarrow A^+ + B + e \quad (3)$$

$$A^+ + B \rightarrow A^- + B^{++} \quad (4)$$

$$A^- + B \rightarrow A + e + B \quad (5)$$

$$A^- + B \rightarrow A^+ + B + 2e \quad (6)$$

The processes 1, 3, 4 may be called charge exchange and 2, the ionisation process. Charge exchange or ionisation in higher charge state may be called stripping reactions.

Processes (1) and (3) are responsible for loss of ions and defocussing of them in an accelerator, thermonuclear reactor or a mass spectrometer, whereas process (2) is useful for space charge neutralisation in the high intensity mass spectrometers. Processes (4) and (6) are important for double acceleration of ions as used with van de Graaf accelerators.

MEASUREMENT OF THE CROSS SECTIONS OF THE INELASTIC COLLISION OF IONS IN GASES

Because of the above applications as well as the physical interest, the measurement and the theoretical calculations of the cross sections of the inelastic collision of different ions with various gases are useful. Several authors[1–3] have reviewed and worked on this subject. Generally, for experimental measurement of such cross sections, one requires ions of selected velocity and preferably of selected mass, which pass through a collision chamber, where collected charge is measured. This method was introduced by Goldman[4] and was, later on, used by Wolf[5], Rostagni[6], Dillon *et al*[7], de Heer[8], Hasted[9] and his co-workers and other authors. Some other methods have been reviewed by Allison[2] and Hasted[1]. We have used the charge

collection method for measurement of the cross section of the process (1). The arrangements, shown in Fig. 1, consists of two condenser plates. The difference in

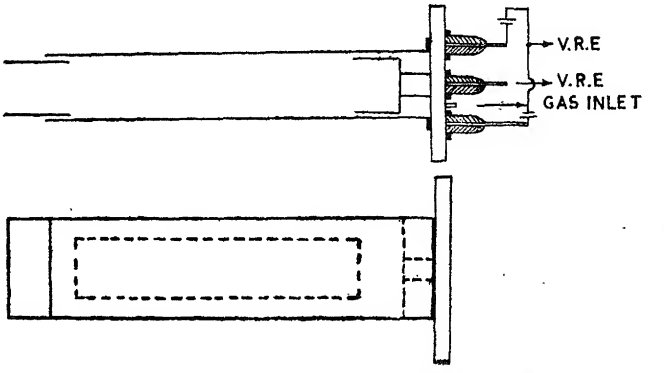

Fig. 1. The collision chamber with the vibrating reed electrometer.

the collected charge in these plates gives the number of slow ions produced by charge exchange. The following formula similar to that given by Ghosh and Sheridan[34], is used for the value of cross section in units of cm^{-1}.

$$Q = \frac{1}{pl} \cdot \frac{I_x}{I_x + I_c} \tag{7}$$

where l = length in cm of the surface on which charge exchange ions are collected,

p = pressure in mm Hg

I_x = current at the charge exchange electrode,

I_c = current at the Faraday chamber.

At sufficiently low pressures, the ratio $[\ I_x\ ]/[\ I_x + I_c\ ]$ is linearly dependent on pressure. $[\ I_x\ ]/[\ I_x + I_c\ ]$ is measured for each energy value at pressures ranging from 6×10^{-5} to 1×10^{-4} mm Hg. The slope of the linear curve for p *vs* $[\ I_x\ ]/[\ I_x + I_c\ ]$ at a certain pressure gives Q for that energy. Figs. 2 and 3 are

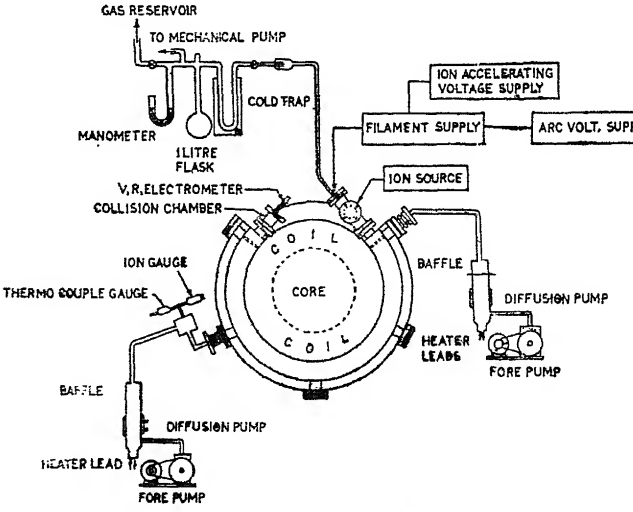

Fig. 2. Schematic diagram of the mass spectrometer,

schematic diagrams of the mass spectrometer and the ion source used by us. The

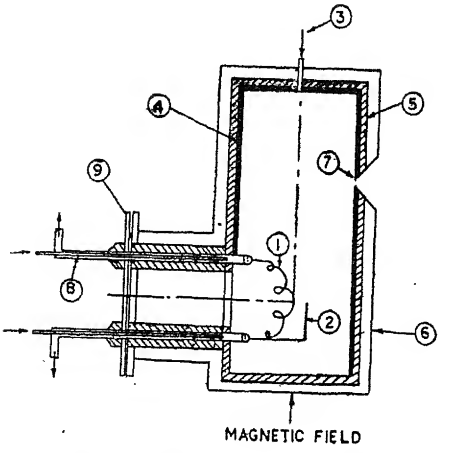

Fig. 3. Details of the ion source.

1. The tungsten filament; 2. The molybdenum plate as electron repeller; 3. Gas inlet and anode lead; 4. Graphite anode; 5. Steatite insulation; 6. Brass container; 7. Ion exit slit; 8. Filament cooling system; 9. Perspex flange for filament leads.

mass spectrometer has been described in the earlier papers.[10] Fig. 4 gives $Q\,(cm^{-1})$ for the reaction

$$Kr^{+} + Kr \rightarrow Kr + Kr^{+}$$

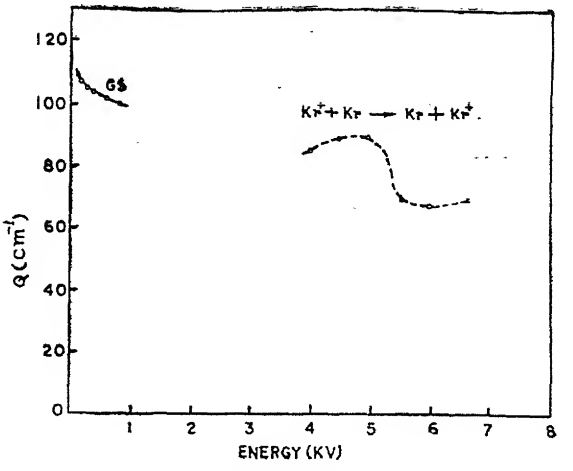

Fig. 4. σ – (ev)$^{\frac{1}{2}}$ curve for Krypton ions in Krypton gas

G S — Experimental results given by Ghosh and Sheridan.

o — Experimental results observed by the author.

measured by us[11] with the above method. Experimental methods and results for other processes are given by different authors. The cross section velocity curves for the above reactions show a general nature for different combinations. Generally,

for the ions and atoms of the same element, the cross section of single electron capture decreases with energy and are called symmetric charge exchange, for all other processes, the maximum shifts to a higher energy than zero. For an asymmetric charge exchange reaction with the ions and the atoms of the different elements, the latter type of curves is obtained.

EXPERIMENTAL RESULTS AND THE ADIABATIC HYPOTHESIS

A qualitative explanation of these curves is given with the adiabatic hypothesis forwarded by Massey and Burhop[3]. With this hypothesis, the resonance maximum of a cross section velocity curve is given by the condition

$$\frac{a \triangle E}{\hbar v} \sim 1 \tag{9}$$

where a is the impact parameter, v, the velocity of the ion, $\triangle E$ the internal energy difference in the interaction, h the Planck's constant.

In the light of this hypothesis, if we consider an asymmetric reaction of electron capture.

$$A^+ + B \rightarrow A + B^+ + \triangle E$$

the resonance of the curve will not be at $v = o$

But for $\triangle E = o$ with a symmetric reaction

$$A^+ + A \rightarrow A + A^+$$

the resonance will occur at $v = o$, so that the cross section will decrease with energy.

Hasted and his co-workers have measured the cross sections for many ion atom combinations. From the results of several experimental and theoretical observations, they[12] have found out an empirical relation between V_{max} and $\triangle E \sqrt{m}$ from a logarithimic plot of $E^{\frac{1}{2}}_{max}$ against $\triangle E \sqrt{m}$ for different reactions shown in Fig. 5. This relation is expressed as

$$\log \sqrt{V}_{max} = 1{\cdot}09 + 1{\cdot}01 \log \triangle E \sqrt{m} \tag{12}$$

From expression (12), the theoretical point for maximum, may be known roughly.

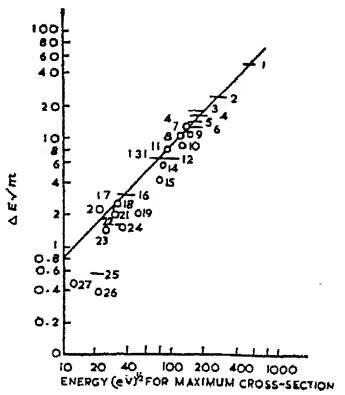

Fig 5. $E\sqrt{m}$ vs $(ev)^{\frac{1}{2}}$; log plot for maximum for different reactions (See Table I) after Hasted.

TABLE—I

1. $He^+ + He \rightarrow He^+ + He^+ + e$; 2. $H^+ + He \rightarrow H^+ + He^+ + e$; 3. $He^+ + H_2 \rightarrow He + H_2^+$; 4. $He^+ + A \rightarrow He + A^+$; 5. $C^+ + H_2 \rightarrow C + H_2^+$; 6. $H_2^+ + He \rightarrow H_2 + He^+$; 7. $H^+ + H \rightarrow H + H^+$; 8. $H^+ + H \rightarrow H(2S) + H^+$; 9. $H^+ + He \rightarrow H + He^+$; 10. $H_2^+ + Ne \rightarrow H_2 + Ne^+$; 11. $H^+ + Ne \rightarrow H + Ne^+$; 12. $He^+ + Kr \rightarrow He + Kr^+$; 13. $H_2^+ + A \rightarrow H_2 + A^+$; 14. $He^+ + Ne \rightarrow He + Ne^+$; 15. $H^+ + Xe \rightarrow H_2 + Xe^+$; 16. $C^+ + Xe \rightarrow C + Xe^+$; 17. $H_2^+ + Xe \rightarrow H_2 + Xe^+$; 18. $Br^+ + Xe \rightarrow Br + Xe^+$; 19. $H^+ + A \rightarrow H + A^+$; 20. $H_2^+ + Kr \rightarrow H_2 + Kr^+$; 21. $N^+ + Kr \rightarrow N + Kr^+$; 22. $O^+ + Kr \rightarrow O + Kr^+$; 23. $H^+ + Xe \rightarrow H + Xe^+$; 24. $H_2^+ + Xe \rightarrow H_2 + Xe^+$; 25. $N_2^+ + A \rightarrow N_2 + A^+$; 26. $H^+ + Kr \rightarrow H + Kr^+$; 27. $H_2^+ + A \rightarrow H_2 + A^+$ (WOLF)

However, in some cases the apparent symmetric cases, such as ions of inert gases with the same atom show asymmetric behaviour. This is not due to the failure of the adiabatic hoyothesis, but due to the difference in their initial and final states, such as $2P_{3/2}$ or $2P_{1/2}$. These two states differ in energy, showing two different ionisation potentials. So, in those cases $\triangle E \neq 0$.

From the empirical relation given in (12) we have $V_{max} \sim 6\ Kv$ for Krypton ions in Krypton when $\triangle E$ is considered to be equal to 0·68 ev, the energy difference between the spin doublet of Kr^+. The experimental V_{max} in Fig. 4 seems to be less than the above value. However, this may be compared with the experimental cross sectional energy curves given by Gilbody and Hasted[13] for A^+ and Ne^+ in the parent gases with Q_{max}, when the energies of the ions are $\sim$ 150 and 10 ev, whereas the above empirical relation gives $E_{max} \sim$ 200 and 25 ev, respectively.

Such discrepancies between the empirical and the experimental curves may be partly understood by assuming that the experimental curve is due to the superposition of the following reactions :

$$Kr^+(2P_{1/2}) + Kr \rightarrow Kr + Kr^+(2P_{3/2}) + 0{\cdot}68 \text{ ev} \quad (13)$$

$$Kr^+(2P_{1/2}) + Kr \rightarrow Kr + Kr^+(2P_{1/2}) \quad (14)$$

$$Kr^+(2P_{3/2}) + Kr \rightarrow Kr + Kr^+(2P_{1/2}) - 0{\cdot}68 \text{ ev} \quad (15)$$

and

$$Kr^+(2P_{3/2}) + Kr \rightarrow Kr + Kr^+(2P_{3/2}) \quad (16)$$

The experimental condition of the source and the collision chamber will determine the fractions of the above reactions, resulting in a spread to the value of V_{max}.

To estimate such fractions a theoretical curve instead of an empirical relation, is required. In the next, we shall discuss a rigorous theory for calculating the cross section for different energy ions.

THEORETICAL CONSIDERATIONS

For collisions of high energy ions with atoms, Born's method has been successfully applied to calculate the elastic or inelastic scattering cross sections for different combinations of ions and atoms. For lower energy ions, the scattered wave method originally applied by Massey and Smith[14] uses a quantum mechanical treatment with the assumption of a distorted wave instead of a plane wave consi-

deration as in the Born's method. Zener[15] has worked out the case of exact resonance, which is directly applicable to the slow collisions of ions with the corresponding neutral atoms which involve transfer of excitation between colliding particles and where a small part of the internal energy is converted to the kinetic energy of the relative motion. Stuckelberg[16] has used an approximate procedure based on the assumption that the relative motion of the colliding particles may be described by classical dynamics, so that the inelastic collision of any ion atom system may be treated. Bates and Massey[17], Magee[18] have considered the charge exchange processes with or without excitation.

Besides these rigorous theories, to the monatomic ion atom systems a simpler theory was necessary to calculate the cross sections of inelastic ion atom collisions for heavier mass range and low energy region. Mott and Frame[19] considered the impact parameter method in detail. Gaunt[20] and Mott[21] use time dependent perturbation theory with $v\,dt = dx$, where v is the velocity of encounter and x is the distance along the zero impact parameter line. This assumes the path of the ions to be a straight line. For energies of the ions greater than the interaction energy between the colliding system, this assumption is true. Mathematically we may express these expressions as

$$R_0\, mv >> \hbar \tag{17}$$

$$R_0\, \triangle p >> \hbar \tag{18}$$

where m is the mass of the ion, v is the velocity and $\triangle p$ is the momentum transfer in the collision.

Secondly, the velocity of ions is sufficiently smaller than that of the atomic electrons, so that adiabatic conditions are almost maintained. The momentum transfer $\triangle p$ in collision, has an order of magnitude V/v, where V is the effective potential energy of interaction, and v is the velocity of ions.

Fig. 6 represents the simple model of collision. Now quantum mechanical method is applied to the system as given by Gurnee and Magee[22].

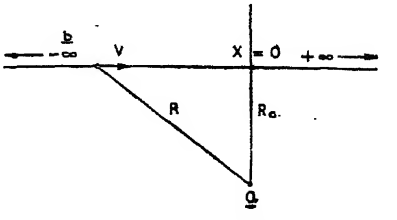

Fig. 6. Model of the collision process.
R_0 – the impact parameter, b – the projectile and a – the target atom or molecule.

If we take the reaction

$$A^+ + A \rightarrow A + A^+ \tag{19}$$

the interaction potential.

$$H' = \frac{1}{R} - \frac{1}{r_b} \tag{20}$$

operated on ψ_{it} for the initial and the final states, gives

$$H_{ti} = \frac{S(R)}{R} - J(R) \tag{21}$$

where

$$S(R) = \langle a \mid b \rangle , \quad J(R) = \langle a \mid \frac{1}{r_b} \mid b \rangle \tag{22}$$

R is the distance between the nucleus of argon ion and the atom r_b the distance between the nucleus of the A^+ and the electron of the atom, with suffixes a, b for the initial and final states. With one electron model of the atom, Gurnee and Magee[22] have used Slater's[23] nodeless wave function as

$$\psi_{it} = N r^{n-1} e^{-\alpha r_{a,b}} \tag{23}$$

where $n = 3$ and the screening constant $\alpha = 1{\cdot}3$ for Argon.

For better agreement with the experimental results, the details of the electronic wave functions are required as shown in Fig. 7, where the wave function of

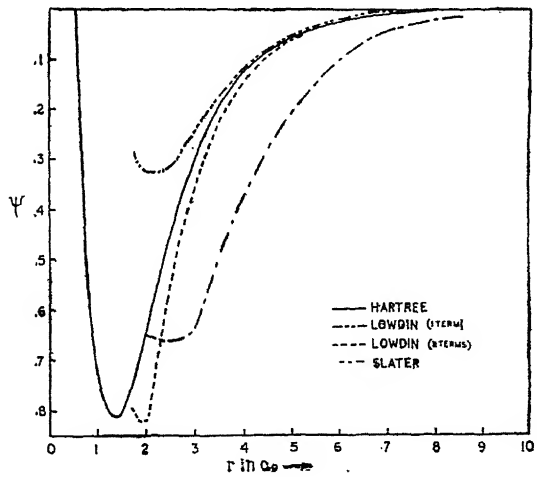

Fig. 7. Comparison of the wave functions at the peripheral region.

Hartree Fock[24] is compared with that of Slater, and first one term and the first terms of the analytical wave functions of Argon given by Lowdin and Appel[25] at the peripheral region.

We use the first term of the Lowdin's wave function for Argon

$$\psi_{it} = A_1 e^{-a_1 r_{a,b}} \tag{24}$$

where $A_1 = -0{\cdot}81754$, $a_1 = 1{\cdot}5080$.

The solution of the integrals (22) gives the probability of the reaction as

$$P(R_o) = \mathrm{Sin}^2 \chi \tag{25}$$

where

$$\chi = \sum_{\nu} \int_{-\infty}^{+\infty} \frac{H_{fi}}{\hbar v} \cos\left(\frac{\triangle Ex}{\hbar v}\right) dx \tag{26}$$

$\triangle E$ is the internal energy involved in the reaction and v is the velocity of the ions.

The numerical value of χ is computed for different values of R_0, the closest distance of collision, and the cross section is obtained graphically from the integral.

$$\sigma = 2\pi \int_0^{\infty} P(R_o)\, R_0\, dR_0 \tag{27}$$

In Fig. 8 (ref. 26) curves I after Gurnee and Magee and II calculated with $\triangle E = 0$, may be compared to show how an analytical wave function gives more accurate results in the low energy range than Slater nodeless wave function.

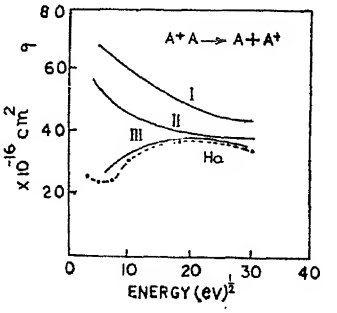

Fig. 8. σ — $(\mathrm{ev})^{\frac{1}{2}}$ curves for Argon ions in Argon gas.
Calculated with (I) Slater's orbital (Gurnee and Magee); with (II) Lowdin's wave function and $\triangle E = 0$, (III) the same and $\triangle E = 0{\cdot}18$ ev.

Curve III is calculated with $\triangle E = 0{\cdot}18$ ev, the energy difference between the spin doublet of A^+. Curve III has a closer agreement with the experimental curve given by Hasted and Gilbody[13] showing the reaction as asymmetric with $\triangle E = 0{\cdot}18$ ev.

Next, we have calculated the cross sections of the reaction[27]

$$A^+ + H_2 \rightarrow A + H_2^+$$

for different energies with the first two terms of the Lowdin's wave function for Argon, i.e.

$$\psi_{it} = A_1 e^{-a_1 r} + A_2 e^{-a_2 r}$$

where $A_1 = -0{\cdot}81754$ $a_1 = 1{\cdot}5080$

$A_2 = -10{\cdot}093$ $a_2 = 2{\cdot}5775$

Of course, the approximation of the first two terms is necessary for a reaction with a higher value of $\triangle E$. The orbitals used for H_2 and H_2^+ are after Wang[32] and Coulson[33], respectively.

In Fig. 9, the curve due to Gurnee and Magee with Slater's wave function is

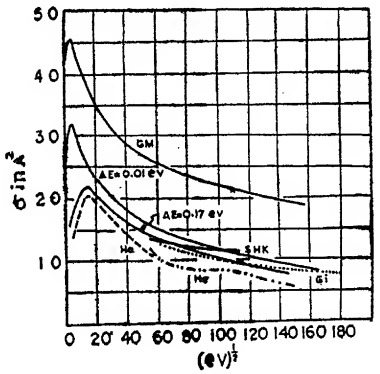

Fig. 9. σ — (ev)$^{\frac{1}{2}}$ curves for Argon ions in hydrogen molecule *G M* — Calculated with Slater's orbital (Gurnee and Magee); $\triangle E = 0{\cdot}01$ ev and $\triangle E = 0{\cdot}17$ ev with Lowdin's wave function calculated by us.
Experimental results observed by Hasted (Ha), Heer (He), Gilbody (Gi), Sluyters *et al* (SHK) are compared.

much higher than those calculated by us. The values of $\triangle E$ given in reference 27 are not correct. For the reactions

$$A^+(2P_{3/2}) + H_2 \rightarrow A + (H_2^{+\prime}) \quad (30)$$

$$A^+(2P_{1/2}) + H_2 \rightarrow A + (H_2^{+\prime}) \quad (31)$$

$$A^+(2P_{1/2}) + H_2 \rightarrow A + H_2^+ \quad (32)$$

$$A^+(2P_{3/2}) + H_2 \rightarrow A + H_2^+ \quad (33)$$

the values of $\triangle E$ are 0·01 ev, 0·17 ev, 0·45 ev, 0·27 ev respectively. Here we have taken the ionisation potential of Argon as 15·69 ev[23] and for H_2 as 15·42 ev[29] as used by Sluyters *et al*[30]. With these values of $\triangle E$, we have calculated the cross sections for different energies for the reactions (30) and (31). The agreement of this curve is much better with the experimental curves given by Hasted and Gilbody[11], Heer[31] and Sluyters *et al*[30].

However, experiments under different conditions may show superposed effects of these types of reactions, happening in different fractions.

It is possible to estimates these fractions from an experimental curve which may be taken as the superposition of the theoretical curves for the reactions, say, (30), (31), (32) and (33).

It is worthwhile to note that with the help of a suitable analytic wave function charge exchange cross sections may be calculated with the preceding method for other ion gas combinations, such as double electron capture by ions to form negative ions and other reactions of a similar nature.

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EXCITATION OF HYDROGEN ATOM IN FAST ENCOUNTER WITH NEGATIVE HYDROGEN ION

By

B. K. GUHA

B. N. College, Patna-4

ABSTRACT

Collision processes involving negative hydrogen ion have drawn attention of a number of workers. In this paper collision of negative hydrogen ion with hydrogen atom, in which the hydrogen atom is excited from initial ground state to $2s$, $2p$ & $3s$ states respectively are studied. Borns' approximation are is used, no account is taken of exchange. Recently Bates and his group have carried out detailed theoritical study of fast collision processes involving proton, hydrogen, and helium atoms. Reasults of our calculation are compared with those of the similar processes involving proton-hydrogen atom and hydrogen-hydrogen atoms from calculation of Bates *et-al*. It is found that at low energy of the incident particle the cross-section approaches to that of the proton-hydrogen atom cross-section for the similar processes. At higher incident energy it approaches to that of proton-hydrogen atom cross-section for $1s$-$2s$ and $1s$-$3s$ excitation processes; but to hydrogen-hydrogen atoms cross-section for $1s$-$2p$ process; while at intermediate energies the cross-section is in-between that of the proton-hydrogen atom and hydrogen-hydrogen atoms case and is charactersed by double peaks.

INTRODUCTION

The negative hydrogen ion in the Suns photo-sphere has long been recognised as responsible for its continuous opacity in the visible range of spectrum. Recently Weinman and co-workers (Weinman, 1955) have produced negative hydrogen ion by passing positive hydrogen ion from a magnetic ion source through a capillary tube containing hydrogen.

Muschlitz-Bally group at University of Florida (Muschlitz-1955) have measured scattering cross-section of low energy negative hydrogen ion in hydrogen and helium respectively using method of Simon and co-workers (Simon-1943). In recent years detailed theoritical study of fast collision processes involving hydrogen and helium atoms and positive ions have been carried out by Bates and his group (Bates: 1953) using Borns' approximation. Considerable interest is attached to the study of the comparable processes involving H^-. The present paper is devoted to the investigation of collision of H^- and hydrogen, where the hydrogen atom is excited to various higher states from the initial ground state by the process. Borns'-approximation is used, no account is taken of exchange: though the range of validity of Borns' approximation in present type of problem is still uncertain.

Problems of similar nature as

$$H^+ + H(1s) \longrightarrow H^+ + H(2s, 2p, 3s)$$

$$H(1s) + H(1s) \longrightarrow H(1s) + H(2s, 4p, 3s)$$

have been studied by Bates Griffing, *et al.*

2. THEORY

We consider collision of a hydrogen atom and a negative hydrogen ion ; both particles being initially in their ground states. Ignoring the effect of the exchange identity of the protons and making use of the Borns' approximation the cross-section of the process for which the hydrogen atom is excited to the states for which the quantum number is *nl*, (the negative ion remaining at the ground state) is given by :

$$Q\ (1s-nl;\ 1s^2) = \frac{8\pi^3\ M^2}{K_i^2\ h^4} \int_{K_{min}}^{K_{max}} |\ N\ |^2\ K\ dK$$

where h is Planck's constant, M is the reduced mass of the system

and $$\bar{K} = \bar{K}_i - \bar{K}_f$$

$$\bar{K}_f = \frac{2\pi\ M\ \bar{V}_f}{h}\ ,\ \bar{K}_i = \frac{2\pi\ M\ \bar{V}}{h}$$

$\bar{V}_i$ and $\bar{V}_f$ are the initial and the final velocities of the relative motion, and :

$$N = \int e^{-i\ \bar{R}.\ \bar{K}_f.}\ \chi^*\ (nl;\ \rho)\ \phi^*\ (1s^2;\ r_1;\ r_2)$$

$$\times \left\{ \frac{e^2}{|\ \bar{R}\ |} - \frac{e^2}{|\ \bar{R}+\bar{\rho}\ |} - \frac{e^2}{|\ \bar{R}-\bar{r}_1\ |} - \frac{e^2}{|\ \bar{R}-\bar{r}_2\ |} + \frac{e^2}{|\ \bar{R}+\bar{\rho}-\bar{r}_1\ |} + \frac{e^2}{|\ \bar{R}+\bar{\rho}-\bar{r}_2\ |} \right\}$$

$$\times\ e^{i\bar{R}\ \cdot\ \bar{K}_i}\ \chi(1s,\rho)\ \phi\ (1s^2;\ r_1;\ r_2)\ \bar{dr}_1\ .\ \bar{dr}_2\ .\ \bar{d\rho}.d\bar{R}$$

where $\bar{R}$ is the relative position vector of the nuclei of the two atoms, $\bar{\rho}$ the position vector of the electron of the hydrogen atom relative to the proton, χ's are the wave function of the hydrogen atom in the state indicated; and r_1, r_2 are the position vectors of the electrons in the negetive hydrogen ion relative to the proton ; Φ being the wave function of the hydrogen ion.

It can be seen that in the integral for 'N'; $\frac{1}{|\ \bar{R}\ |}$; $\frac{1}{|\ \bar{R}-\bar{r}_1\ |}$ and $\frac{1}{|\ \bar{R}-\bar{r}_2\ |}$ do not contribute due to the orthogonality of hydrogen atom wave functions. Therefore we get after integrating :—

$$N = \frac{-a_o^2\ 4\pi e^2}{t^2} \left[\ 1 - \frac{2\cdot 16.\ \alpha^4}{[(2\alpha)^2+t^2]^2}\ \right] \int \chi_{nl}^{*}\ (\rho)\ e^{-ik\cdot\rho}\ \chi\ (\rho)\ d\rho$$

where $t = Ka_o$

so that :

$$Q\ (nl) = \frac{8\pi^3 M^2}{K_i^2\ h^4}\ (4\pi e^2 a_c^{\ 2})^2 \int_{K_{min}}^{K_{max}} \frac{1}{t^4} \left[1 - \frac{2\cdot 16.\alpha^4}{[(2\alpha)^2 + t^4]^2}\ \right]^2\ I_{n1}^{\ 2}\ K.dK$$

where

$$I_{nl} = \int \chi_{nl}^{*}(\rho)\, e^{-ik\rho}\, \chi_{is}(\rho)\, d\rho$$

$$\text{therefore } Q(nl) = \frac{8\pi^3 M^2}{K_i^2 h^4} \times \frac{16\pi^2 e^4 a_o^4}{a_o^2} \int_{K_{min}}^{K} \frac{1}{t^4} \left[1 - \frac{2\cdot 16\cdot \alpha^4}{[(2\alpha)^2 + t^4]^2}\right]^2 I_{nl}^2\, t.dt$$

$$= \frac{8\pi^3 M^2}{\left(\frac{2\pi}{h} M v_i\right)^2 h^4} \times \frac{16.\pi^2 e^4 a_o^4}{a_o^2} \int_{K_{min}}^{K_{max}} \left[1 - \frac{2\cdot 16.\alpha^4}{[(2\alpha)^2 + t^4]^2}\right]^2 I_{nl}^2\, t^{-3}\, dt$$

$$= \frac{4c^2}{v_i^2} \times \left(\frac{2\pi e^2}{hc}\right)^2 \int_{t_{min}}^{t_{max}} \left[1 - \frac{2\cdot 16.\alpha^4}{[(2\alpha)^2 + t^2]^2}\right]^2 I_{nl}^2\, t^{-3}\, dt$$

Now

$$t_{max} = a_o K_{max} = a_o (K_i + K_f)$$

$$t_{min} = a_o K_{min} = a_o (K_i - K_f)$$

As is usual in the treatment of heavy particle collisions, it is sufficient to take t_{max} as infinite (Bates and Griffing 1953) and if $\triangle E$ is the difference in energy between the two states for a perticular excitation processes then

$$t_{min} = a_o K_{min} = \frac{2\bar{A}\triangle E}{\hbar v_i}\left[1 + \frac{\triangle E}{2M v_i^2}\right]$$

2·2. For discrete transitions I can be calculated from (4) by elementry methods they have been tabulated by Bates and Griffing, we quote their value :

$$I(1s - 2s) = \frac{2^{17/2} \cdot t^2}{(4t^2 + 9)^3}$$

$$I(1s - 2p) = \frac{2^{15/2} \cdot 3t}{(4t^2 + 9)^3}$$

$$I(1s - 3s) = \frac{2^4 \cdot 3^{7/2}(27t^2 + 16).t^2}{(9t^2 + 16)^4}$$

On substituing them in (5) one can obtain analytical epressions for cross-sections. But they are in general cumbersome and are very tedious to evaluate. It is much easier to evalute the integrals numerically, which is actually done in this paper.

2·3. It can be seen from the expression for cross-section

$$Q(1s-nl) = \frac{4c^2}{v_i^2}\left(\frac{2\pi e^2}{hc}\right)^2 \int_{t_{min}}^{t_{max}} \left\{1 - \frac{2\cdot 16.\alpha^4}{[(2\alpha)^2 + t^2]^2}\right\}^2 I(1s-nl)^2 \times t^{-3}\, dt$$

that if

$$\frac{2\cdot 16.\alpha^4}{[(2\alpha)^2 + t^2_{min}]^2} << 1$$

then the expression for the cross-section becomes

$$Q\,(1s - nl) = \frac{4c^2}{v_i^2}\left(\frac{2\pi e^2}{hc}\right)^2 \int_{t_{min}}^{t_{max}} I\,(1s - nl)^2\; t^{-3}\, dt$$

which is the same as that of the excitation of hydrogen atom by proton. Thus the screening of the negative hydrogen ion has no effect on scattering if the incident energy is below certain value. If we take as first approximation

$$t_{min} = \frac{a_0 \Delta E}{\hbar v_i} \times 2\pi$$

it follows that for $(1s-2s)$ and $(1s-2p)$ transitions the hydrogen atom-hydrogen ion cross-section will differ from hydrogen atom-hydrogen positive ion (proton) cross-section provided incident energy is greater than 563ev.

3. RESULTS

The cross-sections associated with the processes mentioned in the introduction were computed from the formula that have been given. Figures 1 to 3 show

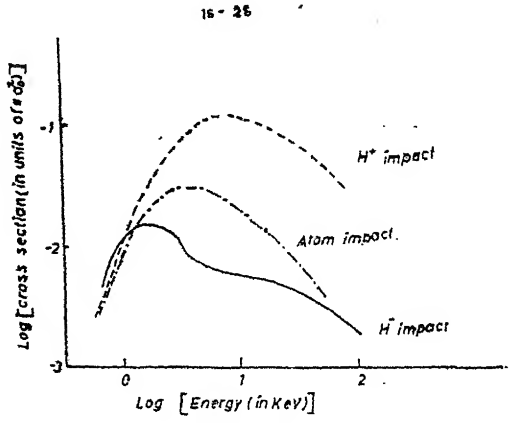

Fig. 1. $H^+ + H(1s) \rightarrow H^+ + H(2s)$ - - -
$H(1s) + H(1s) \rightarrow H(1s) + H(2s)$ -o-o-
$H^-(1s^2) + H(1s) \rightarrow H^-(1s^2) + H(2s)$ ——— } Bates and Griffing

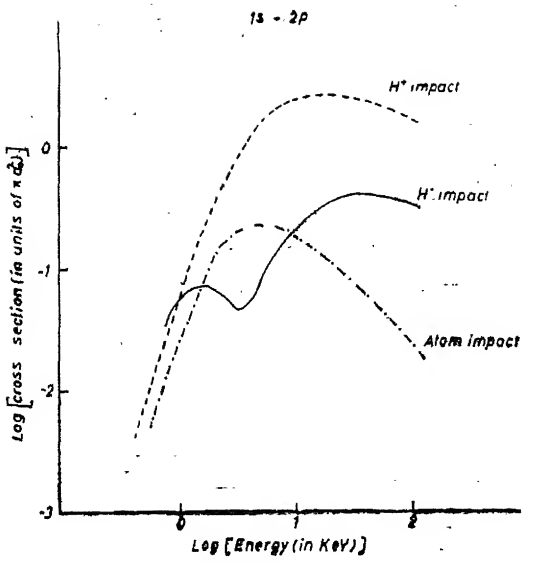

Fig. 2. $H^+ + H(1s) \rightarrow H^+ + H(2p)$ - - -
 $H(1s) + H(1s) \rightarrow H(1s) + H(2p)$ -o-o-
 $H^- (1s^2) + H(1s) \rightarrow H^-(1s^2) + H(2p)$ ——— } Bates and Griffing

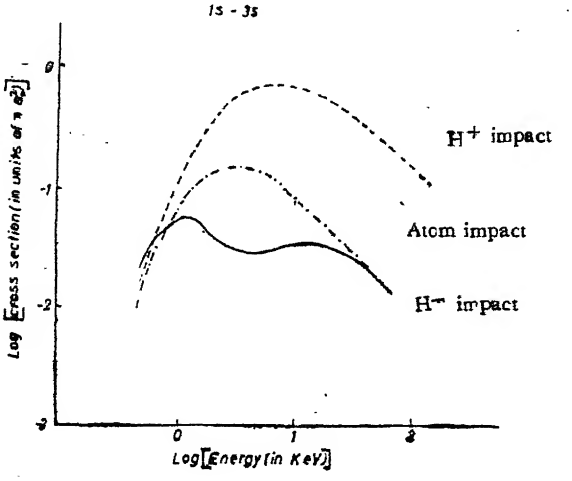

Fig. 3. $H^+ + H(1s) \rightarrow H^+ + H(3s)$ - - -
 $H(1s) + H(1s) \rightarrow H(1s) + H(3s)$ -o-o-
 $H^-(1s^2) + H(1s) \rightarrow H^-(1s^2) + H(3s)$ ——— } Bates and Griffing

the values obtained. It should be noted that a log-log scale is used, and that the independent variable chosen is not E, the energy of relative motion, but instead the energy of the incident particle, the atom undergoing transition being taken

to be at rest. For comparison the cross-section of proton-hydrogen atom and hydrogen-hydrogen atom as calculated by Bates and Griffing are also plotted in the same figures.

On comparing the cross-section curve of ($H-H^-$) with corresponding curves for (p - H) and (H – H) respectively it will be observed that at low energy the cross-section of ($H-H^-$) impact lies closed to but above the cross-section of the latter processes. When energy is sufficiently low the ($H-H^-$) cross-section almost coincides with that of (p - H) impact. This is in conformity with the trend observed in (p - H) and (H—H) impact.

The curve for ($H-H^-$) is characterised by two maximum, some what similar to the double peaks observed by Moiseiwtsch and Steward (Moiseiwtsch and Steward – 1954) in collision between hydrogen and helium atoms. Moiseiwtsch attributed the phemomena to double transition. Essentially the same shape of curve is obtained by Bates and Griffing, who, however, remarks that to a more accurate approximation in the lower part of the energy region concerned, the first maximum may be pertially suppressed and that the true curve may conceivably show a single broad maxima.

For ($1s-2s$) and ($1s-3s$) excitation the maximum cross-section is below that of the corresponding (H – H) cross-section and is shifted to considerable lower energy. But for ($1s-2p$) transition the maximum cross-section is in-between that of (H - H) and ($p-H$) cross-section and is at higher energy.

At higher energy the curve for ($1s-2s$) and ($1s-3s$) transitions almost coincides with that of the (H - H) curve for the corresponding transitions ; while the curve for ($1s-2p$) transition lie above (H – H) curve and has a tendency to coincide with (p - H) curve from below.

Unfortunately no experiment is done in the energy region of this calculation. Only available data is due to E. E. Muschlit who measured the scattering cross-section of H^- in hydrogen and helium in the energy range 4*ev.* to 300*ev.*

ACKNOWLEDGMENTS

I should like to express my gratitude to Dr. H. N. Yadav, for many helpful discussions. My thanks are also due to Prof. L. M. Chatterjee, Prof. of Physics, Patna University, for granting every facility to carry out the investigation.

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CROSS SECTION FOR DISSOCIATIVE RECOMBINATION OF NITRIC OXIDE*

By

J. J. GIBBONS *and* B. E. SQUIRES, Jr.

Ionosphere Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania, U. S. A.

ABSTRACT

An attempt is made to set up a model for the calculation of the cross section for dissociative recombination of No^+, namely the reaction

$$NO^+ + e^- \longrightarrow N + O.$$

In this reaction it is assumed that a nitric oxide molecular ion in its ground state $(^1\Sigma^+)$ captures a free electron of low energy and splits up into two neutral atoms in the state

$$N\ (^2D) + O\ (^3P)$$

The calculation of such cross sections is of particular interest in considerations involving the D-region of the ionosphere. The reaction is broken up by assuming the existence of an intermediate state NO* which invariably decays into N and O. Time-dependent first order perturbation theory is then used to calculate the cross section for the reaction

$$NO^+ + e^- \longrightarrow NO^*.$$

The method follows to a large extent that outlined by Bauer and Wu[7], but differs from this work in several important particulars. The previous work is discussed and criticized. Using quite rough approximations at the end of the calculation it was found that the cross section for 1 ev. electrons is of the order of 12×10^{-16} cm^2.

I. INTRODUCTION

Formulating a Theory for the Ionosphere :

It is clear that any understanding of the ionosphere must involve an understanding of the processes of charge formation and dissipation. In elementary terms the electronic charge formation is due largely to solar radiation, and this charge is dissipated largely through the process of recombination with positive ions.

In formulating a detailed theory of the ionosphere it is of considerable interest to know the relative importance of the various processes of recombination. If these processes can be accurately formulated, the conditions for equilibrium may be imposed to calculate ionospheric parameters such as the electron density. In the D-and lower E-ionospheric layers the difficulty of interpreting observable data by radio frequency propagation techniques makes the knowledge of the recombination process all the more interesting. In obtaining such knowledge, not only the types of processes mut be known, but since each such process proceeds at a rate varying with the type and concentration of the reactants, the particular atoms, ions, and molecules involved must be determined.

Present State of Recombination Theory :

Havens *et al.*[1] considered three types of processes affecting the recombination rate in the F2 region :

* The research reported in this paper has been sponsored by the Geophysical Research Directorate of the Air Force Cambridge Research Laboratory, under Contract AF 19 (604)-4563.

1. Dissociative recombination :

$$e^- + O_2^+ \longrightarrow O' + O''$$

2. Photo-recombination :

$$e^- + O^+ \longrightarrow O + h\nu$$

3. Charge exchange :

$$O^+ + O_2 \longrightarrow O_2^+ + O$$

Recent studies[2] of the ionosphere over Fort Churchill, Canada, using three Aerobee-Hi rockets, identically instrumented with Bennett radio-frequency ion-mass spectrometers, have shown that even under varying conditions a substantial portion of the ions present in the lower ionosphere have an atomic mass of 30. Considering the constituents present at these altitudes, there appears little doubt that these ions are in fact NO^+.

Bates[3] has shown that dissociative recombination is a process occurring at a much faster rate than the other recombination processes involving electrons. However Harteck and Dondes[4] considered that dissociative recombination is effective only to an extent of 10 to 20%, and that the most important process must be the photo-recombination of NO^+. Nicolet and Aikin[5] agree with Bates that dissociative recombination is the most important process, but admit that the dissociative recombination coefficient of NO^+ ions is not known. There are apparently no experimental data for this reaction.[6]

Statement of the Problem :

This work will illustrate with a model calculation how the cross section of NO^+ for the process

$$e^- + NO^+ \longrightarrow N + O$$

of dissociative recombination may be estimated from theoretical considerations. By this reaction is meant that a thermal electron incident upon an NO^+ ion neutralizes the excess charge and causes the nuclei to dissociate. The resulting atoms may be either in their ground or an excited state.

Previous Calculation of Dissociative Recombination :

The only previous theoretical calculation in this field known to the author is a paper by Bauer and Wu[7] published in 1956, and hereinafter referred to as B and W. B and W present a model for the reaction

$$e^- + H_2^+ \longrightarrow H' + H''$$

In attempting to apply their model to the calculation under consideration here, considerable difficulties were occasionally encountered. In several instances it has proved possible to overcome these difficulties but, in general, the present author makes no claim that this model is complete in detail, nor certainly that any numerical answer at this stage of development has a particular useful significance.

II. METHOD

Reduction of the Reaction into a Simpler One :

We wish to estimate the cross section of the reaction

$$e^- + NO^+ \longrightarrow N + O \tag{1}$$

in which the collision between an electron of thermal energy and a nitric oxide ion in its ground electronic and vibrational state leads to an oxygen and a nitrogen atom in their ground or excited states. Following the proposal of B and W we shall regard this as a two-stage process consisting of the capture of the electron by the ion NO^+ to give a nitric oxide molecule in an excited "rotational-vibrational" level in the continuum of an excited electronic state, which we shall regard as metasable,

$$e^- + NO^+ \longrightarrow NO^* \tag{2}$$

and the subsequent dissociation of this molecule into two neutral atoms in their ground or excited states,

$$NO^* \longrightarrow N + O \tag{3}$$

Generally, instead of this last reaction, it is conceivable that the system might proceed backward, the neutral nitric oxide molecule ejecting an electron,

$$NO^* \longrightarrow NO^+ + e^- \tag{4}$$

but such a reaction is quite similar to the Auger transition in atoms, and since Auger transitions have a probability considerably below that which would be expected for the separation of two repulsive atoms, we shall neglect this possibility. Our problem may, therefore, be reduced to calculating the capture cross section of NO^+ for a thermal electron.

Time-Dependent Perturbation Theory :

Essentially, this capture reaction involves the transition of an electron in the continuum of the NO^+ field into a bound state. Such transitions may often be treated using time-dependent perturbation theory[5]. In time-dependent perturbation theory we assume that the Hamiltonian for the electronic wave function of the system may be broken up into the sum of two terms, one of which is time independent. Mathematically, this is expressed by letting

$$H = H^\circ + H'(t) \tag{5}$$

It is also assumed that the solution of

$$H^\circ \psi_n = i\hbar \frac{\partial \psi_n}{\partial t} \tag{6}$$

is known exactly, and can be expressed as

$$\psi_n = u_n e^{-\frac{iE_n t}{\hbar}} \tag{7}$$

where the u_n is a complete set of orthonormal functions satisfying the relation

$$H^\circ u_n = E_n u_n \tag{8}$$

The problem we wish to solve is expressed by

$$H\psi = i\hbar \frac{\partial \psi}{\partial t} \tag{9}$$

If we expand the unknown wave function ψ in terms of the set of known functions, and carry through the indicated operations, we find for the relation among the coefficients $a_n(t)$

$$\frac{d}{dt} a_m(t) = \frac{1}{i\hbar} \sum_n a_n(t)\, e^{-\frac{i(E_n - E_m)t}{\hbar}} \int u_m \overset{*}{H}'(t)\, u_n\, d\tau \tag{10}$$

The perturbation procedure is introduced by assuming that the integral on the right

$$H'_{mn}(t) = \int u_m^* H'(t)\, u_n\, d\tau \tag{11}$$

is "small" and inserting the arbitrary parameter λ:

$$H'(t) \longrightarrow \lambda H'(t) \qquad a_n(t) \longrightarrow \sum_j a_n^{(j)} \lambda^j \tag{12}$$

For the first order we have that

$$\frac{d}{dt} a_m^{(1)} = \frac{1}{i\hbar} \sum_n a_n^{(o)}\, e^{-\frac{i(E_n - E_m)t}{\hbar}} H'_{mn}(t) \tag{13}$$

If we then suppose that at time $t = 0$ only the j th state is occupied,

$$a_n^{(o)} = \delta_{nj} \tag{14}$$

and that the Hamiltonian $H'(t)$ is independent of time except for being turned on at time $t = 0$ and off at time t, the time integration may be completed. The result is

$$a_m^{(1)}(t) = -\frac{2iH'_{mi}}{E_j - E_m}\, e^{-\frac{i(E_j - E_m)t}{\hbar}} \sin \frac{(E_j - E_m)t}{2\hbar} \tag{15}$$

To calculate the transition probability we let $\rho(E)\, dE$ be the number of possible final states between E and $E + dE$. The total probability for transition to any final state is then

$$\int_{-\infty}^{\infty} \left| a_f^{(1)}(t) \right|^2 \rho_f(E_j)\, dE_j \tag{16}$$

and the transition probability, P, is the time derivative of this quantity,

$$P = \frac{2\pi}{\hbar} \left| H'_{fj} \right|^2 \rho(E_j) \tag{17}$$

Although first-order perturbation theory is not expected to be accurate in the range of thermal electron velocities, we will ignore this limitation for the purpose of obtaining a' raugh approximation. In practical cases, it is difficult to set up a workable criterion for the validity of this approximation, although useful results are likely to be obtained when the speed of the electron is large in comparison with e^2/h [8,9].

Specification of the Hamiltonian :

We must now specify how the Hamiltonian for the electronic wave function can be separated so that the wave function for the initial state can be written in terms of an eigenfunction of an unperturbed Hamiltonian, and so that the perturbation is manageable. We shall treat the following system as the complete Hamiltonian

$$H = \frac{\hbar^2}{2}\left(\frac{\nabla_A^2}{M_A} + \frac{\nabla_B^2}{M_B}\right) - \frac{\hbar^2}{2m_e}\sum_{i=1}^{15}\nabla_i^2 - e^2\sum_{i=1}^{15}\left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iA}}\right) + e^2\sum_{i=1}^{14}\sum_{j=i+1}^{15}\frac{1}{r_{ij}} + \frac{Z_A Z_B e^2}{R_{AB}} \tag{18}$$

where r_{iA} is the distance between the i th electron and nucleus A, r_{iB} is the distance between the i th electron and nucleus B, r_{ij} is the distance between the i th and j th electrons, and R_{AB} is the internuclear distance.

Ideally, we are thinking in terms of an incident plane wave electron with thermal velocity, distorted by the field of a singly charged ion, being captured by this ion, and forming the metastable molecule heretofore mentioned. In the separation of this Hamiltonian we make only a slight extension of the idea suggested by B and W. The process under consideration is a rearrangement collision, and it is necessary to define the zeroth-order Hamiltonian H^o and the perturbation H' in such a way that the perturbation formula (17) is valid.

One way is to choose the states u_m and u_n to be eigenstates of the same Hamiltonian so that the wave functions u_m, u_n are orthogonal. Accordingly, we select the following system as the unperturbed Hamiltonian :

$$H^o = -\frac{\hbar^2}{2}\left(\frac{\nabla_A^2}{M_A} + \frac{\nabla_B^2}{M_B}\right) - \frac{\hbar^2}{2m_e}\sum_{i=1}^{15}\nabla_i^2 - e^2\sum_{i=1}^{15}\left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}}\right) + e^2\sum_{i=1}^{13}\sum_{j=i+1}^{14}\frac{1}{r_{ij}} + \frac{Z_A Z_B e^2}{R_{AB}} \tag{19}$$

The interaction of the incident electron with the bound electrons of NO^+ is regarded as the perturbation

$$H' = e^2\sum_{i=1}^{14}\frac{1}{r_{i_{15}}} \tag{20}$$

In effect we are presuming here that for the initial state we may neglect the detailed interactions of the incident electron with the bound electrons of NO^+. In this formulation for the states u_m and u_n we shall defined the state ψ_B of NO^* as one representing fifteen bound elctrons, one electron of which has the peculiar property that it does not interact with the other fourteen, and define ψ_C of $NO^+ + e^-$ as a state representing fourteen electrons in the normal state of NO^+ and the other electron in the continuum in the field of two nuclei. At first sight this separation of the Hamiltonian of the system into $H^0 + H'$ seems strange, but it has the advantage of satisfying the orthogonality requirement mentioned above, and is accordingly free from such difficulty as the prior-post ambiguity which is associated with the use of non-orthogonal states in the usual treatment of rearrangement collisions.[7]

However, in separating the Hamiltonian in this manner we introduce an enhancement of the calculated cross section due to the fact that in this formulation the incident electron apparently sees a charge of $+15e$ instead of simply $+e$. The factor thus introduced can be removed.[9] For this case of a thermal electron incident on a heavy ion, this enhancement multiplies the result by a factor of about 15.

A simple argument may be given to show that it is indeed the interaction of the electrons which would be expected to be the perturbing influence. Suppose, for instance, that the perturbation is turned off, so that in the above formulation we would expect no transition probability. We will now consider the case of the incident electron passing in the neighborhood of the NO^+ ion even so. In this case the two nuclei are in some sense bound together, namely, by the total configuration of the fourteen electrons, but the incident electron is not permitted to interact with these electrons. Since it is not permitted to interact with these electrons, it cannot disturb their configuration. Hence also it cannot disturb the bond of the two nuclei. In this case, then, it would appear that classically the incident electron would proceed in an appropriate hyperbolic path or, if sufficiently close, a corresponding path for the two center problem.

The type of process we are interested in considering here is, in fact, just such an interaction between the incident and the bound electrons. This interaction is to change the state of the outer bound electrons and the incident electron in such a manner that the repulsive orbitals dominate the bonding orbitals.

Application of Perturbation Theory :

To find the transition probability for the capture of an electron into a bound state from the continuum state, we first consider the reverse process, namely,

$$NO^* \rightarrow NO^+ + e^- \tag{4}$$

the excitation of an electron from a bound state into the continum. From time-dependent perturbation theory, equation (17), we have that

$$P_{BC} = \left(\frac{2\pi}{\hbar} \right) \left| \int \psi_C^* \, H' \, \psi_B \, d\tau \right|^2 \rho \, (E) \tag{21}$$

The density of states ρ E is given by

$$\rho(E) = \frac{2m_e \hbar k V d\omega}{(2\pi\hbar)^3} \tag{22}$$

where $\hbar k$ is the momentum of the incident electron whose wave function is normalized in the volume V.

The number of states dN lying in the volume element $\vec{dk}$ is

$$dN = \frac{2V}{(2\pi)^3} \vec{dk} \tag{23}$$

the factor 2 arising from the number of spin states. If we write

$$\vec{dk} = k^2 dk d\omega = k^2 dk \sin\theta \, d\theta \, d\phi \tag{24}$$

and note that since

$$k^2 = \frac{2m_e E}{\hbar^2} \tag{25}$$

and

$$dk = \frac{m_e}{\hbar\sqrt{2m_e E}} dE \tag{26}$$

we find that

$$dN = \frac{m_e k V}{4\pi^3\hbar^2} dE d\omega \tag{27}$$

is the number of states between E and E+dE within the solid angle $d\omega$. The total number of states with momentum at least k is

$$\int_0^k dN = \int_V^k 2 \frac{V}{(2\pi)^3} k^2 dk d\omega = \frac{2V}{8\pi^3} \cdot \frac{4}{3} \pi k^3 = \frac{Vk^3}{3\pi^2} \tag{28}$$

The probability per second of the capture of an electron of momentum $\hbar k$ is then obtained by dividing P_{BC} by the total number of states and multiplying by the multiplicity (2S +1) of the bound electronic state, namely,

$$P_{CB} = \frac{3m_e (S+1)}{2k^2\hbar^3} \left| \int \psi_C^* H' \psi_B \, d\tau \right|^2 d\omega \tag{29}$$

The total cross section is obtained by dividing P_{CB} by the incident flux, $\hbar k/mV$, and integrating over all directions ω. Like B and W we shall ignore any dependence of the matrix element on the direction of k. We then obtain

$$\sigma_C = \frac{6\pi m_e^2 V (2S+1)}{k^3\hbar^4} \left| \int \psi_C^* H' \psi_B \, d\tau \right|^2 \tag{30}$$

Eigenvalues of the Unperturbed Hamiltonian :

Since the mass of the electrons is small compared to that of the nuclei, we may regard this transition as a "vertical" Franck-Condon transition. That is, we assume that the electron transition in the molecule takes place so rapidly in comparison to the vibrational motion that, immediately afterwards, the nuclei still have very nearly the same relative position and velocity as before the transition.

To make a calculation of this capture cross section we therefore need to know the electronic energies of the zeroth-order Hamiltonian in the form of potential energy curves as a function of the nuclear separation R_{AB}. Since our zero-order Hamiltonian does not include the interaction of one of the electrons with the others, the eigenstates of H^0 are not the eigenstates of NO; however we may use the same spectroscopic notation. To clarify matters, we shall use the notation "NO" when referring to the fictitious eigenstates of H^0, and simply NO for the real eigenstates of nitric oxide. To find the eigenstates of "NO" we neglect the exchange integrals with the last electron and take the eigenstates of NO^+, obtained from spectroscopic date, add the eigenstates of a three body system consisting of a nitrogen nucleus, an oxygen nucleus, and one electron, and subtract the nuclear-nuclear interaction energy which has been counted twice

$$E(\text{"NO"}) = E(NO^+) + E(N^{+7} - O^{+8} - e^-) - \frac{Z_A Z_{B^e}{}^2}{R_{AB}} \tag{31}$$

The eigenvalues of the three body system are determined by means of a variational calculation. The details of this calculation are now set forth.

III. EIGENVALUES OF A THREEBODY SYSTEM

Formulation of the Problem :

In this section we give a method for calculating the approximate eigenvalues of a three body system consisting of two unlike nuclei and one electron. The calculation was performed by a variational method,[10] and as we will now show, all of the required integrals may be expressed analytically by transforming to confocal elliptical coordinates. The actual numerical computations for this calculation were carried out using a Basic IBM 650 electronic computer. In forming the wave functions for the variational calculation, linear combinations of atomic orbitals of K-and L- electrons were used. The extension to higher orbitals is quite obvious and would lead to somewhat more accurate results.

Let ψ be the electronic wave function of this system, r_A and r_B the distances from these nuclei, respectively, and r_{AB} the internuclear distance. The electronic wase equation is

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi + \left(\frac{Z_{A^e}{}^2}{r_A} - \frac{Z_{B^e}{}^2}{r_B} + \frac{Z_A Z_{B^e}{}^2}{R_{AB}}\right)\psi = E\psi \tag{32}$$

where m_e is the mass of an electron, and $\hbar$ is Planck's constant divided by 2π.

As a variational wave function we use a linear combination of the corresponding hydrogenic wave functions centered alternately on the two nuclei :

$$\phi_k = \sum_{\alpha}^{M} C_{k\alpha}\, \chi_\alpha \tag{33}$$

where

$$\left.\begin{aligned}
\chi_1 &= u_{1sA} = \frac{1}{\sqrt{4\pi}} \left(\frac{Z_A}{a_0}\right)^{3/2} .2e^{-Z_A \frac{r_A}{a_0}} \\
\chi_2 &= u_{1sB} = \frac{1}{\sqrt{4\pi}} \left(\frac{Z_B}{a_0}\right)^{3/2} .2e^{-Z_B \frac{r_B}{a_0}} \\
\chi_3 &= u_{2sA} = \frac{1}{\sqrt{4\pi}} \left(\frac{Z_A}{a_0}\right)^{3/2} \frac{\left(2 - Z_A \frac{r_A}{a_0}\right)}{2\sqrt{2}} e^{-\frac{Z_A}{2}\frac{r_A}{a_0}} \\
\chi_4 &= u_{2sB} = \frac{1}{\sqrt{4\pi}} \left(\frac{Z_B}{a_0}\right)^{3/2} \frac{\left(2 - Z_B \frac{r_B}{a_0}\right)}{2\sqrt{2}} e^{-\frac{Z_B}{2}\frac{r_B}{a_0}} \\
\chi_5 &= u_{2p\,(0)A} = \frac{\sqrt{2}}{8\sqrt{\pi}} \left(\frac{Z_A}{a_0}\right)^{5/2} r_A\, e^{-\frac{Z_A}{2}\frac{r_A}{a_0}} \cos\theta \\
\chi_6 &= u_{2p\,(0)B} = \frac{\sqrt{2}}{8\sqrt{\pi}} \left(\frac{Z_B}{a_0}\right)^{5/2} r_B\, e^{-\frac{Z_B}{2}\frac{r_B}{a_0}} \cos\theta \\
\chi_7 &= u_{2p\,(-1)A} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z_A}{a_0}\right)^{5/2} r_A\, e^{-\frac{Z_A}{2}\frac{r_A}{a_0}} e^{-i\phi} \sin\theta \\
\chi_8 &= u_{2p\,(-1)B} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z_B}{a_0}\right)^{5/2} r_B\, e^{-\frac{Z_B}{2}\frac{r_B}{a_0}} e^{-i\phi} \sin\theta \\
\chi_9 &= u_{2p\,(1)A} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z_A}{a_0}\right)^{5/2} r_A\, e^{-\frac{Z_A}{2}\frac{r_A}{a_0}} e^{i\phi} \sin\theta \\
\chi_{10} &= u_{2p\,(1)B} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z_B}{a_0}\right)^{5/2} r_B\, e^{-\frac{Z_B}{2}\frac{r_B}{a_0}} e^{i\phi} \sin\theta
\end{aligned}\right\} \tag{34}$$

In general we may write

$$\chi_\alpha = \frac{C_\alpha}{\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{\rho_\alpha}{2}}\, \rho_\alpha^{l_\alpha}\, L_{n_\alpha + l_\alpha}^{2l_\alpha + 1}(\rho_\alpha)\, P_{l_\alpha}^{m_\alpha}(\cos\theta_\alpha)\, e^{i m_\alpha \phi} \tag{35}$$

where

$$C_\alpha = -\left[\left(\frac{2Z_\alpha}{n_\alpha}\right)^3 \frac{(n_\alpha - l_\alpha - 1)!\ (2l_\alpha + l)\ (l_\alpha - |m_\alpha|)!}{4n_\alpha \left\{(n_\alpha + l_\alpha)!\right\}^3 (l_\alpha + |m_\alpha|)!}\right]^{1/2} \tag{36}$$

and

$$\rho_\alpha = \frac{2Z_\alpha}{n} \frac{r_\alpha}{a_0} \tag{37}$$

and that

$$L^{2l_\alpha + 1}_{n_\alpha + l_\alpha}(\rho_\alpha) = \sum_{k=0}^{n_\alpha - l_\alpha - 1} g_{\alpha k} \left(\frac{n_\alpha}{Z_\alpha D}\right)^k \rho_\alpha^k \tag{38}$$

where

$$g_{\alpha k} = (-1)^{k+1} \frac{\left\{(n_\alpha + l_\alpha)!\right\}^2}{(n_\alpha - l_\alpha - 1 - k)!\,(2l_\alpha + 1 + k)!\,k!} \left(\frac{Z_\alpha D}{n_a}\right)^k \tag{39}$$

Here n, l, and m are the usual hydrogen wave function quantum numbers. Notice that by selecting the Z−axis of the co-ordinate system in the direction from nucleus A to nucleus B it is not necessary to distinguish the co-ordinate ϕ in the co-ordinate systems centered on A and B; respectively.

We define the matrix elements

$$H_{\alpha\beta} = \int \chi_\alpha^* H \chi_\beta \, d\tau \tag{40}$$

and

$$\Delta_{\alpha\beta} = \int \chi_\alpha^* \chi_\beta \, d\tau \tag{41}$$

The enery is given in the usual manner by

$$E_k = \frac{\int \phi_k^* H \phi_k \, d\tau}{\int \phi_k^* \phi_k \, d\tau} = \frac{\sum_{\beta\alpha}\sum C_{k\beta} C_{k\alpha} H_{\alpha\beta}}{\sum_{\beta\alpha}\sum C_{k\beta} C_{k\alpha} \Delta_{\alpha\beta}} \tag{42}$$

Then

$$E_k \sum_{\alpha\beta}\sum C_{k\alpha} C_{k\beta} \Delta_{\alpha\beta} = \sum_{\alpha\beta}\sum C_{k\alpha} C_{k\beta} H_{\alpha\beta} \tag{43}$$

and

$$\frac{\partial E_k}{\partial C_{k\gamma}} \sum_{\alpha\beta}\sum C_{k\alpha} C_{k\beta}\Delta_{\alpha\beta} + E_k \frac{\partial}{\partial C_{k\gamma}}\left(\sum_{\alpha b}\sum C_{k\alpha} C_{k\beta}\Delta_{\alpha\beta} \right)$$

$$= \frac{\partial}{\partial C_{k\gamma}}\left(\sum_{\alpha\beta}\sum C_{k\alpha} C_{k\beta} H_{\alpha\beta} \right) \tag{44}$$

For the energy to be a minimum, $\partial E_k/\partial C_{k\gamma}$ must be zero for all γ.

$$E_k \frac{\partial}{\partial C_{k\gamma}}\left(\sum_{\alpha\beta}\sum C_{k\alpha} C_{k\beta}\Delta_{\alpha\beta}\right) = \frac{\partial}{\partial C_{k\gamma}}\left(\sum_{\alpha\beta}\sum C_{k\alpha} C_{k\beta} H_{\alpha\beta}\right) \tag{45}$$

or

$$E_k \sum_{\alpha} C_{k\alpha}\Delta_{\alpha r} = \sum_{\alpha} C_{k\alpha} H_{\alpha\gamma} \tag{46}$$

for all γ. This represents a set of simultaneous linear homogeneous equations in the independent variables $C_{k\alpha}$

$$\sum_{\alpha} C_{k\alpha}\left(H_{\alpha\beta} - \Delta_{\alpha\beta} E_k \right) = 0 \tag{47}$$

for all β. In order that this set have a non-trival solution it is necessary that the determinant of the coefficients vanish

$$\begin{vmatrix} H_{11}-\Delta_{11}E & H_{12}-\Delta_{12}E & H_{13}-\Delta_{13}E & \cdots\cdots & H_{1,10}-\Delta_{1,10}E \\ H_{21}-\Delta_{21}E & H_{22}-\Delta_{22}E & \cdots\cdots & \cdots\cdots & H_{2,10}-\Delta_{3,10}E \\ H_{31}-\Delta_{31}E & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ H_{10,1}-\Delta_{10,1}E & H_{10,2}-\Delta_{10,2}E & \cdots\cdots & \cdots\cdots & H_{10,10}-\Delta_{10\,10}E \end{vmatrix} = 0 \tag{48}$$

In the next four portions of this sections we shall show how the elements of this matrix may be calculated.

GENERAL CONSIDERATIONS

All of the integrals here under consideration may be put into an analytical form by means of a transformation into confocal elliptical coordinates. This transformation is given by the equations

$$\mu = \frac{r_\alpha + r_\beta}{a_0 D} \qquad r_\alpha = \frac{\mu + \nu}{2} a_0 D$$

$$\nu = \frac{r_\alpha - r_\beta}{a_0 D} \qquad r_\beta = \frac{\mu - \nu}{2} a_0 D \tag{49}$$

$$\phi = \phi \qquad \phi = \phi$$

where

$$D = \frac{R_{AB}}{a_0} \tag{50}$$

and it is understood that the subscripts α and β here refer to different nuclei. The transformation of the angular coordinate θ will be determined by that center to which the angle is referred. If the polar center is at the reference α, then

$$r_\beta^2 = r_\alpha^2 + R_{AB}^2 - 2 r_\alpha R_{AB} \cos\theta_\alpha \tag{51}$$

$$\cos\theta_\alpha = - \frac{r_\beta^2 - r_\alpha^2 - R_{AB}^2}{2 r_\alpha R_{AB}}$$

Letting

$$a = \frac{R_{AB}}{2} \tag{52}$$

$$\cos\theta_\alpha = \frac{a^2(\mu - \nu)^2 - a^2(\mu + \nu)^2 - 4a^2}{4a^2(\mu + \nu)}$$

$$\cos\theta_\alpha = \frac{\mu\nu + 1}{\mu + \nu} \tag{53}$$

and

$$\sin\theta_\alpha = \sqrt{1 - \cos^2\theta_\alpha} = \frac{\sqrt{(\mu+\nu)^2 - (\mu\nu - 1)^2}}{\mu + \nu}$$

$$\sin\theta_\alpha = \frac{\sqrt{\mu^2 + \nu^2 - \mu^2\nu^2 - 1}}{\mu + \nu} \tag{54}$$

A diagram of these angles is shown in Figure 1. Likewise if the polar center is at reference β, then

$$r_\alpha^2 = r_\beta^2 + R_{AB}^2 + 2 r_\beta R_{AB} \cos\theta_\beta \tag{55}$$

$$\cos\theta_\beta = \frac{\mu\nu - 1}{\mu - \nu} \tag{56}$$

$$\sin\theta_\beta = \frac{\sqrt{\mu^2 + \nu^2 - \mu^2\nu^2 - 1}}{\mu - \nu} \tag{57}$$

The element of volume in these coordinates is given by

$$d\tau = \frac{a_0{}^3 D^2}{8} (\mu^2 - \nu^2)\, d\mu\, d\nu\, d\phi \tag{58}$$

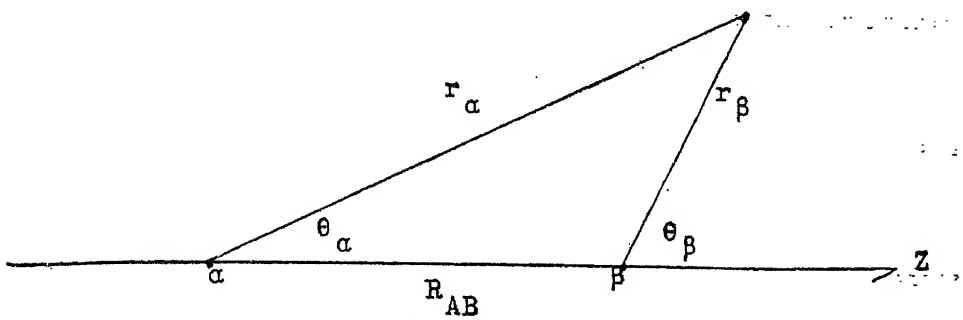


Figure 1. Angles in polar and elliptical coordinates.

and the ranges of integration over all space are

$$\int_1^\infty d\mu \quad \int_{-1}^{1} d\nu \quad \int_0^{2\pi} d\phi \tag{59}$$

In these coordinates we may write

$$\rho_\alpha = \frac{Z_\alpha D}{n_\alpha} (\mu + \nu)\,; \rho_\beta = \frac{Z_\beta D}{n_\beta} (\mu - \nu) \tag{60}$$

$$L^{2l_\alpha + 1}_{n_\alpha + l_\alpha} (\rho_\alpha) = \sum_{k=0}^{n_\alpha - l_\alpha - 1} g_{\alpha k} (\mu+\nu)^k$$

$$L^{2l_\beta + 1}_{n_\beta + l_\beta} (\rho_\beta) = \sum_{k=0}^{n_\beta - l_\beta - 1} g_{\beta k} (\mu-\nu)^k \tag{61}$$

It will presenty be shown that each of these integrals, which can thus be reduced to analytical forms, are linear combinations of special cases of the general type

$$\Lambda(a, b, M, N, P, Q) \equiv \int_1^\infty d\mu e^{-a\mu} \int_{-1}^{1} d\nu e^{-b\nu} (\mu+\nu)^M (\mu-\nu)^N P_\mu P_\nu Q \tag{62}$$

In order to write a general analytical function representing the value of this integral, it is convenient first to define the functions

$$f_\mu (a, n) = \int_1^\infty \mu^n e^{-a\mu} d\mu = \frac{n! e^{-a}}{a^{n+1}} \sum_{k=0}^{n} \frac{a^k}{k!} \tag{63}$$

and

$$f_\nu\ (a,n) = \int_{-1}^{1} \nu^n e^{-a\nu} d\nu = \frac{n!}{a^{n+1}} \sum_{k=0}^{n} \left\{ e^a \frac{(-a)^k}{k!} - e^{-a} \frac{a^k}{k!} \right\} \tag{64}$$

Next we take note that

$$(\mu+\nu)^M = \sum_{j=0}^{M} \binom{M}{j} \mu^{M-j} \nu^j \tag{65}$$

and

$$(\mu-\nu)^N = \sum_{k=0}^{N} (-1)^k \binom{N}{k} \mu^{N-k} \nu^k \tag{66}$$

so that

$$(\mu+\nu)^M (\mu-\nu)^N \mu^P \nu^Q =$$

$$\sum_{j=0}^{M} \binom{M}{j} \sum_{k=0}^{N} (-1)^k \binom{N}{k} \mu^{M+N+P-j-k} \nu^{Q+j+k} \tag{67}$$

It is therefore apparent that

$$\Lambda(a, b, M, N, P, Q)$$
$$= \sum_{j=0}^{M} \binom{M}{j} \sum_{k=0}^{N} (-1)^k \binom{N}{k} \left[f_\mu (a, M+N+P-j-k) f_\nu (b, Q+j+k) \right] \tag{68}$$

The Diagonal Elements :

If we define W_α by means of the hydrogen-like wave equation

$$-\frac{\hbar^2}{2m_e} \nabla^2 \chi_\alpha - \frac{Z_\alpha e^2}{r_\alpha} \chi_\alpha = W_\alpha \chi_\alpha \tag{69}$$

then

$$H_{\alpha\alpha} = \int \chi_\alpha\ ^*\left(W_\alpha - \frac{Z_\beta e^2}{r_\beta} + \frac{Z_A Z_B e^2}{R_{AB}}\right) \chi_\alpha\, d\tau$$

$$= W_\alpha + J_\alpha + \frac{Z_A Z_B e^2}{a_0 D} \tag{70}$$

where

$$J_\alpha = \int \chi_\alpha^* \left(-\frac{Z_\beta e^2}{r_\beta}\right) \chi_\alpha\, d\tau \tag{71}$$

Here, as before, it is understood that the subscripts α and β refer to different nuclear centers. Using the relations we have already derived, we can now write

$$J_\alpha = \frac{c_\alpha^{\,2}}{2\pi a_0^{\,3}} \int e^{-\rho_\alpha} \rho_\alpha^{\,2l_\alpha} \left\{ \begin{matrix} 2l_\alpha + 1 \\ L \\ n_\alpha + l_\alpha \end{matrix} (\rho_\alpha) \; P_{l_\alpha}^{|m_\alpha|} (\cos\theta_\alpha) \right\}^2 \left(\frac{-Z_\beta e^2}{r_\beta} \right) d\tau$$

$$= \left(\frac{e^2}{2a_0^{\,4}} \right) \frac{4C_\alpha^{\,2} Z_\beta}{2\pi D} \left(\frac{Z_\alpha D}{n_\alpha} \right)^{2l_\alpha} \tag{72}$$

$$\int e^{-\frac{Z_\alpha D}{n_\alpha}(\mu+\nu)} \frac{(\mu+\nu)}{(\mu-\nu)}^{2l_\alpha} \left\{ \sum_{k=0}^{n_\alpha - l_\alpha - 1} g_{ak} (\mu+\nu)^k P_{l_\alpha}^{|m_\alpha|} (\cos\theta_\alpha) \right\}^2 d\tau$$

Let

$$B_\alpha = -\tfrac{1}{2} C_\alpha^{\,2} Z_\beta D^2 Q_\alpha^{\,2l_\alpha} \tag{73}$$

where

$$Q_\alpha = \frac{Z_\alpha D}{n_\alpha} \tag{74}$$

So that

$$J_\alpha = \left(\frac{e^2}{2a_0} \right) \frac{B_\alpha}{2\pi} \int\int\int e^{-Q_\alpha(\mu+\nu)} (\mu+\nu)^{2l_\alpha+1} \left\{ L(\rho) P(\cos\theta_\alpha) \right\}^2 d\mu d\nu d\phi \tag{75}$$

Integrating over the angular variable ϕ,

$$J_\alpha = \left(\frac{e^2}{2a_0} \right) B_\alpha \int_1^\infty d\mu\, e^{-Q_\alpha \mu} \int_{-1}^{1} d\nu\, e^{-Q_\alpha \nu} (\mu+\nu)^{2l_\alpha+1} \left\{ \sum_{k=0}^{i_\alpha} g_{ak} (\mu+\nu)^k \right\}^2 \left\{ P_{l_\alpha}^{|m|} (\cos\theta_\alpha) \right\}^2 \tag{76}$$

where

$$i_\alpha = n_\alpha - l_\alpha - 1 \tag{77}$$

then

$$J_\alpha = \left(\frac{e^2}{2a_0}\right) B_\alpha \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\alpha} g_{\alpha k} \int_1^\infty d\mu\, e^{-Q_\alpha \mu} \int_{-1}^{1} dv\, e^{-Q_\alpha \nu} (\mu+\nu)^{2l_\alpha + k + j + 1} \left\{ P_l^{|m|} \right\}^2 \tag{78}$$

We now consider this by cases:

CASE I. s—states $l = m = 0$

$$(P_0^0)^2 = 1$$

$$J_\alpha = \left(\frac{e^2}{2a_0}\right) B_\alpha \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\alpha} g_{\alpha k} \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,0,0) \tag{79}$$

CASE II. p—states $l = 1$

A. $|m| = 0$

$$\left\{ P_1^0(\cos\theta_\alpha) \right\}^2 = \cos^2\theta_\alpha = \frac{(\mu\nu+1)^2}{(\mu+\nu)^2}$$

$$J_\alpha = \left(\frac{e^2}{2a_0}\right) B_\alpha \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\alpha} g_{\alpha k} \left\{ \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,2,2) + 2\Lambda(Q_\alpha, Q_\alpha, k+j+1,0,1,1) + \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,0,0) \right\} \tag{80}$$

B. $|m| = 1$

$$\left\{ P_1^1(\cos\theta_\alpha) \right\}^2 = \sin^2\theta_\alpha = \frac{\mu^2+\nu^2-\mu^2\nu^2-1}{(\mu+\nu)^2}$$

$$J_\alpha = \left(\frac{e^2}{2a_0}\right) B_\alpha \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\alpha} g_{\alpha k} \left\{ \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,2,0) + \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,0,2) - \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,2,2) - \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,0) - \Lambda(Q_\alpha, Q_\alpha, k+j+1,0,0,0) \right\} \tag{81}$$

Finally, we make note of the fact that $\triangle_{\alpha\alpha} = 1$ for all α.

The Non-diagonal Elements $\triangle_{\alpha\beta}$:

In using the symbol $\triangle_{\alpha\beta}$ as a general term in the non-diagonal elements, we have no assurance that α and β here refer to distinct nuclei. However, if they should refer to the same nucleus, then we see from the orthogonality of the

hydrogen-like wave functions that that term would vanish. Hence in our further considerations here we shall assume that the α and β refer to distinct nuclei. It is also easy to see that the $\Delta_{\alpha\beta}$ terms are symmetric with respect to an interchange of indices, i. e., $\Delta_{\alpha\beta} = \Delta_{\beta\alpha}$.

In discussing this integral, we see that we will in general be involved with two distinct hydrogen-like wave functions, each with its own set of quantum numbers. Hence the subscripts on the quantum numbers will have an important meaning. However, since the angular variable ϕ remains untransformed in changing to confocal elliptical coordinates, it is clear that $\Delta_{\alpha\beta} = 0$ if $m_\alpha \neq m_\beta$. Therefore we may hereafter omit the subscript on that quantum number

$$\Delta_{\alpha\beta} = \frac{C_\alpha C_\beta}{2\pi a_0^3} \int e^{-\frac{1}{2}(\rho_\alpha + \rho_\beta)} \rho_\alpha^{l_\alpha} \rho_\beta^{l_\beta} L_{n_\alpha + l_\alpha}^{2l_\alpha+1}(\rho_\alpha) L_{n_\beta + l_\beta}^{2l_\beta+1}(\rho_\beta) \quad (82)$$

$$P_{l_\alpha}^{|m|}(\cos\theta_\alpha) P_{l_\beta}^{|m|}(\cos\theta_\beta)\, d\tau$$

The exponent may be rewritten as

$$\begin{aligned} \tfrac{1}{2}(\rho_\alpha + \rho_\beta) &= \tfrac{1}{2}\left\{ \left(\frac{Z_\alpha D}{n_\alpha} + \frac{Z_\beta D}{n_\beta} \right) \mu + \left(\frac{Z_\alpha D}{n_\alpha} - \frac{Z_\beta D}{n_\beta} \right) \nu \right\} \\ &= \tfrac{1}{2}\left\{ (Q_\alpha + Q_\beta)\mu + (Q_\alpha - Q_\beta)\nu \right\} \qquad (83) \\ &= S_{\alpha\beta}\mu + T_{\alpha\beta}\nu \end{aligned}$$

where

$$S_{\alpha\beta} = \tfrac{1}{2}(Q_\alpha + Q_\beta) \text{ and } T_{\alpha\beta} = \tfrac{1}{2}(Q_\alpha - Q_\beta) \qquad (84)$$

Hence

$$\Delta_{\alpha\beta} = \frac{C_\alpha C_\beta Q_\alpha^{l_\alpha} Q_\beta^{l_\beta}}{2\pi a_0^3} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k}$$

$$\int e^{-S_{\alpha\beta}\mu - T_{\alpha\beta}\nu} (\mu+\nu)^{l_\alpha + j} (\mu-\nu)^{l_\alpha + k} P_{l_\alpha}^{|m|}(\cos\theta_\alpha) P_{l_\beta}^{|m|}(\cos\theta_\beta)\, d\tau$$

$$= E_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \int_1^\infty d\mu \int_{-1}^{1} d\nu\, e^{-S_{\alpha\beta}\mu - T_{\alpha\beta}\nu} \qquad (85)$$

$$(\mu+\nu)^{l_\alpha + j + 1} (\mu-\nu)^{l_\alpha + k + 1} P_{l_\alpha}^{|m|}(\cos\theta_\alpha) P_{l_\beta}^{|m|}(\cos\theta_\beta)$$

where

$$E_{\alpha\beta} = \frac{C_\alpha C_\beta Q_\alpha^{\,l_\alpha} Q_\beta^{\,l_\beta} D^3}{8} \tag{86}$$

CASE I. s-states $l_\alpha = l_\beta = 0$

$$P_o^{\,o} = 1$$

$$\Delta_{\alpha\beta} = E_{\alpha\beta} \sum_{j=o}^{i_\alpha} g_{\alpha j} \sum_{k=o}^{i_\beta} g_{\beta k}\, \Lambda (S_{\alpha\beta},\ T_{\alpha\beta},\ j+1, k+1, 0, 0) \tag{87}$$

CASE II. Mixed states $l_\beta = 0,\ l_\alpha \neq 0, m = 0$

We are interested only in the case where $l_\alpha = 1$

$$P_1^{\,o} (\cos \theta_\alpha) = \frac{\mu\nu + 1}{\mu + \nu}$$

$$\Delta_{\alpha\beta} = (-1)^{\beta} E_{\alpha\beta} \sum_{j=o}^{i_\alpha} g_{\alpha j} \sum_{k=o}^{i_\beta} g_{\beta k} \left\{ \Lambda (S_{\alpha\beta},\ T_{\alpha\beta},\ j+1, k+1,\ 1,\ 1) + \Lambda (S_{\alpha\beta},\ T_{\alpha\beta},\ j+1, k+1,\ 0, 0) \right\} \tag{88}$$

CASE III. p-states $l_\alpha = l_\beta = 1$

A. $m = 0$

$$P_1^{\,o} (\cos \theta_\alpha) = \frac{\mu\nu + 1}{\mu + \nu} \qquad P_1^{\,o} (\cos \theta_\beta) = \frac{\mu\nu - 1}{\mu - \nu}$$

$$\Delta_{\alpha\beta} = E_{\alpha\beta} \sum_{j=o}^{i_\alpha} g_{\alpha j} \sum_{k=o}^{i_\beta} g_{\beta k} \left\{ \Lambda (S_{\alpha\beta},\ T_{\alpha\beta},\ j+1, k+1, 2, 2) - \Lambda (S_{\alpha\beta},\ T_{\alpha\beta},\ j+1, k+1, 0, 0) \right\} \tag{89}$$

B. $|m| = 1$

$$P_1^{\,1} (\cos \theta_\alpha) = \sin \theta_\alpha = \frac{\sqrt{\mu^2 + \nu^2 - \mu^2\nu^2 - 1}}{\mu + \nu}$$

$$P_1^{\,1} (\cos \theta_\beta) = \sin \theta_\beta = \frac{\sqrt{\mu^2 + \nu^2 - \mu^2\nu^2 - 1}}{\mu - \nu}$$

$$\Delta_{\alpha\beta} = E_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \Big\{ \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j+1, k+1, 2, 0)$$

$$+ \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j+1, k+1, 0, 2) - \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j+1, k+1, 2, 2)$$

$$- \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j+1, k+1, 0, 0) \tag{90}$$

The Non-diagonal Elements $H_{\alpha\beta}$

We consider now $H_{\alpha\beta}$ with $a \neq \beta$

$$H_{\alpha\beta} = \int \chi_\alpha^* \left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Z_A e^2}{r_A} - \frac{Z_B e^2}{r_B} + \frac{Z_A Z_B e^2}{R_{AB}} \right) \chi_\beta \, d\tau \tag{91}$$

Suppose first that, although $\alpha \neq \beta$, α and β represent hydrogen-like wave functions centered on the same nucleus. For continuity with the previous sections, let us rename χ_β as χ_γ and the subscript α denote the nucleus in question, and the subscript β the other nucleus

$$H_{\alpha\gamma} = \int \chi_\alpha^* \left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Z_\alpha e^2}{r_\alpha} - \frac{Z_\beta e^2}{r_\beta} + \frac{Z_A Z_B e^2}{R_{AB}} \right) \chi_\gamma \, d\tau \tag{92}$$

$$= \int \chi_\alpha^* \left(W_\gamma - \frac{Z_\beta e^2}{r_\beta} + \frac{Z_A Z_B e^2}{R_{AB}} \right) \chi_\gamma \, d\tau$$

But since χ_α and χ_β are orthogonal, we have in this instance

$$H_{\alpha\gamma} = K_{\alpha\gamma} = \int \chi_\alpha^* \left(-\frac{Z_\beta e^2}{r_\beta} \right) \chi_\gamma \, d\tau \tag{93}$$

Now since the angular variable ϕ is untransformed by the change into confocal elliptical coordinates, and does not appear in the operator, $K_{\alpha\gamma}$ 0 if $m_\alpha \neq m_\beta$. Hence we will consider here only those cases where $m_\alpha = m_\gamma = m$. It is also clear from the above equation that in these instances where the two functions are centered on the same nucleus that $K_{\alpha\gamma} = K_{\gamma\alpha}$.

$$K_{\alpha\gamma} = -\frac{C_\alpha C_\gamma}{2\pi a_0^3} Z_\beta e^2 \int e^{-\rho_\alpha} \rho_\alpha^{\alpha + l_\gamma} L_{n_\alpha + l_\alpha}^{2l_\alpha + 1} (\rho_\alpha) L_{n_\gamma + l_\gamma}^{2l_\gamma + 1} (\rho_\gamma)$$

$$P_{l_\alpha}^{|m|} (\cos\theta_\alpha) P_{l_\gamma}^{|m|} (\cos\theta_\gamma) \frac{1}{r_\beta} \, d\tau$$

$$= \left(\frac{e^2}{2a_0} \right) F_{\alpha\gamma} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\gamma} g_{\gamma k} \int_1^\infty d\mu \int_{-1}^{1} d\nu \; e^{-Q_\alpha (\mu+\nu)} (\mu+\nu)^{l_\alpha + l_\gamma + 1}$$

$$P_{l_\alpha}^{|m|} (\cos\theta_\alpha) \; P_{l_\gamma}^{|m|} (\cos\theta_\alpha) \tag{94}$$

where

$$F_{\alpha\gamma} = -\tfrac{1}{2} \; C_\alpha \; C_\gamma \; Z_B \; Q_\alpha^{\,l_\alpha + l_\gamma} \; D^2 \tag{95}$$

CASE I. s-states $l_\alpha = l_\gamma = 0$

$$K_{\alpha\gamma} = \left[\frac{e^2}{2a_0} \right] F_{\alpha\gamma} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\gamma} g_{\gamma k} \left\{ \Lambda (Q_\alpha, Q_\alpha, 1, 0, 0, 0) \right\} \tag{96}$$

CASE II. Mixed states $l_\alpha = 0, l_\gamma = 1$

$$P_1^{\,0} (\cos\theta_\alpha) = \frac{\mu\nu + 1}{\mu + \nu}$$

$$K_{\alpha\gamma} = \left(\frac{e^2}{2a_0} \right) F_{\alpha\gamma} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\gamma} g_{\gamma k} \left\{ \Lambda (Q_\alpha, Q_\alpha, 1, 0, 1, 1) + \right.$$

$$\left. \Lambda (Q_\alpha, Q_\alpha, 1, 0, 0, 0) \right\} \tag{97}$$

We now need consider only cases of $H_{\alpha\beta}$ where χ_α and χ_β are hydrogen-like wave functions referring to different nuclei. Here we may write immediately

$$H_{\alpha\beta} = \int \chi_\alpha^* \left(W_\beta - \frac{Z_\alpha e^2}{r_\alpha} + \frac{Z_A Z_B e^2}{R_{AB}} \right) \chi_\beta \; d\tau$$

$$= \Delta_{\alpha\beta} W_\beta + K_{\alpha\beta} + \frac{Z_A Z_B e^2 \Delta_{\alpha\beta}}{a_0 D} \tag{98}$$

where

$$K_{\alpha\beta} = \int \chi_\alpha^* \left(- \frac{Z_\alpha e^2}{r_\alpha} \right) \chi_\beta \; d\tau \tag{99}$$

Our problem now is to evaluate this last integral. It is readily seen that in these instances $K_{\alpha\beta} \neq K_{\beta\alpha}^*$ if one considers, for instance, K_{12} and K_{21} since $Z_A \neq Z_B$. As before, the angular variable ϕ is untransformed and does not

appear in the operator, so that $K_{\alpha\beta} = 0$ if $m_\alpha \neq m_\beta$. Hence we need only to consider those cases where $m_\alpha = m_\beta = m$.

$$K_{\alpha\beta} = -\frac{C_\alpha\, C_\beta\, Z_\alpha\, e^2}{2\pi a_0^{\,3}} \int \frac{1}{r_\alpha}\, e^{-\frac{1}{2}(\rho_\alpha + \rho_\beta)}\, \rho_\alpha^{\,l_\alpha}\, \rho_\beta^{\,l_\beta}\, L_{n_\alpha + l_\alpha}^{2l_\alpha + 1}(\rho_\alpha)$$

$$L_{n_\beta + l_\beta}^{2l_\beta + 1}(\rho_\beta)\; P_{l_\alpha}^{|m|}(\cos\theta_\alpha)\; P_{l_\beta}^{|m|}(\cos\theta_\beta)\, d\tau$$

$$K_{\alpha\beta} = \left(\frac{e^2}{2a_0}\right) F_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \int_1^\infty$$

$$d\mu \int_{-1}^{1} d\nu\; e^{-S_{\alpha\beta}\mu - T_{\alpha\beta}\nu}\, (\mu+\nu)^{l_\alpha + j}$$

$$(\mu - \nu)^{l\beta + k + 1}\, P_{l_\alpha}^{|m|}(\cos\theta_\alpha)\; P^{|m|}(\cos\theta_\beta) \qquad (100)$$

where

$$F_{\alpha\beta} = -\tfrac{1}{2}\, C_\alpha\, C_\beta\, Z_\alpha\, D^2\, Q_\alpha^{\,l_\alpha}\, Q_\beta^{\,l_\beta} \qquad (101)$$

CASE I. s—states $l_\alpha = l_\beta = 0$

$$K_{\alpha\beta} = \left(\frac{e^2}{2a_0}\right) F_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k}\, \Lambda(S_{\alpha\beta},\, T_{\alpha\beta},\, j,\, k+1,\, 0,\, 0) \qquad (102)$$

CASE II. Mixed States $l_\alpha = 0$, $l_\beta = 1$ or $l_\alpha = 1$, $l_\beta = 0$

$$P_1^0(\cos\theta_{\alpha\,(\beta)}) = \frac{\mu\nu \pm 1}{\mu \pm \nu}$$

$$K_{\alpha\beta} = \left(\frac{e^2}{2a_0}\right) F_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \left\{ \Lambda(S_{\alpha\beta},\, T_{\alpha\beta},\, j,\, k+1,\, 1,\, 1) \right.$$

$$\left. + (-1)^{1\beta}\, \Lambda(S_{\alpha\beta},\, T_{\alpha\beta},\, j,\, k+1,\, 0,\, 0) \right\} \qquad (103)$$

CASE III. p—states $l_\alpha = 1$, $l_\beta = 1$

A. $m=0$

$$K_{\alpha\beta} = \left(\frac{e^2}{2a_0}\right) F_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \int_1^\infty d\mu \int_{-1}^{1} dv\, e^{-S_{\alpha\beta}\mu - T_{\alpha\beta}\nu}$$

$$(\mu - \nu)^j \ (\mu - \nu)^{k+1} \ (\mu\nu + 1)(\mu\nu - 1)$$

$$= \left(\frac{e^2}{2a_0}\right) F_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \left\{ \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j, k+1, 2, 2) \right.$$

$$\left. - \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j, k+1, 0, 0) \right\} \qquad (104)$$

B. $|m| = 1$

$$K_{\alpha\beta} = \left(\frac{e^2}{2a_0}\right) F_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \int_1^\infty d\mu \int_{-1}^{1} dv\, e^{-S_{\alpha\beta}\mu - T_{\alpha\beta}\nu}$$

$$(\mu + \nu)^j \ (\mu - \nu)^{k+1} \ (\mu^2 - 1)(1 - \nu^2)$$

$$= \left(\frac{e^2}{2a_0}\right) F_{\alpha\beta} \sum_{j=0}^{i_\alpha} g_{\alpha j} \sum_{k=0}^{i_\beta} g_{\beta k} \left\{ \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j, k+1, 2, 0) \right.$$

$$+ \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j, k+1, 0, 2) - \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j, k+1, 2, 2)$$

$$\left. - \Lambda (S_{\alpha\beta}, T_{\alpha\beta}, j, k+1, 0, 0) \right\} \qquad (105)$$

Results of this Calculation :

Tabe I gives the approximate eigenvalues of the first ten electronic states of an $N^{+7} - O^{+8} - e^-$ system in units of $e^2/2a_0$ as a function of the internuclear distance D in units of a_0.

TABLE 1

Eigenvalues of the $N^{+7} - O^{+8} - e^-$ System

State	D = 1	D = 1½	D = 2	D = 2½	D = 3
$\sigma 1s_O$	25·9	−4·5	−21·0	−31·4	−38·3
$\sigma 1s_N$	41·8	9·2	−7·68	−18·1	−25·1
	76·7	46·8	31·7	22·5	16·2
$\pi 2p_O$	82·72	49·62	33·16	23·28	16·72
$\bar{\pi} 2p_O$	82·72	49·62	33·16	23·28	16·72
	85·0	50·7	34·6	25·4	19·2
$\pi 2p_N$	87·56	52·59	36·01	26·27	19·82
$\bar{\pi} 2p_N$	87·56	52·59	36·01	26·27	19·82
	88·6	57·4	40·3	30·3	24·1
		61·4	43·5	34·2	28·2

These results are plotted in Figure 2. If we now remove the energy of the nuclear interaction, $56e^2/R_{AB}$, we obtain the results shown in Figure 3.

$$E' = E(N^{+7} - O^{+8} - e^-) - \frac{56e^2}{R_{AB}} = E(\text{"NO"}) - E(NO^+) \qquad (106)$$

These curves thus express the difference in energy between "NO" and the corresponding state of NO^+ where the state of the electron in "NO" not appearing in NO^+ is determined by the particular curve. The given curves could be identified by carrying out the calculation so that their asympote became clear. In the absence of these data, we can in general only conjecture which curves correspond to which states. It is quite clear, however, that the two lowest states are $\sigma 1s$.

Furthermore, it is not difficult to show that the $\sigma 1s$ state on oxygen lies lower than the $\sigma 1s$ state on nitrogen.[11] To do this we need consider that the molecular orbital is a linear combination of $\sigma 1s$ orbitals only.

$$\psi = c_O \psi_O (1s) + c_N \psi_N (1s)$$

The secular equation is

$$\begin{vmatrix} H_{OO} - E & H_{NO} - \Delta_{NO}E \\ H_{NO} - \Delta_{NO} E & H_{NN} - E \end{vmatrix} = O$$

where the symbols have their usual meaning. We imagine the internuclar distance to be sufficiently large so that the overlap integral Δ_{NO} may be taken equal to zero. The energy eigenvalues, given by the solution of the secular equation, are

$$E = \tfrac{1}{2}\left\{\left(H_{OO} + H_{NN}\right) \pm \sqrt{\left(H_{OO} - H_{NN}\right)^2 + 4H_{NO}^2}\right\}$$

For $H_{OO} = H_{NN}$, the upper sign gives $c_O = c_N$; the lower sign gives $c_O = -c_N$. For $H_{OO} > H_{NN}$ we may therefore conclude that the upper sign corresponds to the case where c_O and c_N have the same sign; the lower sign corresponds to the case where c_O and c_N have opposite signs. For the limiting case where $H_{NO} = 0$, the upper sign gives $E = H_{OO}$, the lower sign gives $E = H_{NN}$.

Likewise we can identify the $\pi 2p$ states, for in this calculation there are no non-diagonal matrix elements involving $\pi 2p$ orbitals except those between $\pi 2p$ orbitals. We thus have a situation quite like the $\sigma 1s$ case, i.e., the secular equation is of the second decree, and, as before, the $\pi 2p$ orbital on oxygen lies lowest.

IV. DETAILED FORMULATION OF THE CALCULATION

Configuration of the Reaction :

In figure 4 are reproduced the potential energy curves of NO and NO^+ as a function of internuclear distance as obtained from spectroscopic data.[12] From these curves it appears that the transition in resonance with the ground state of NO^+ and a thermal electron is the $B^2\pi$ state of NO, which would in this case subsequently dissociate into $N(^2D)$ and $O(^3P)$ due to the excess kinetic energy. The configuration of the expected reaction is thus as follows

$$NO^+ \left[(\sigma 1s_O)^2 (\sigma 1s_N)^2 (\sigma 2s_O)^2 (\sigma 2s_N)^2 (\sigma 2p_O) (\sigma 2p_N) (\pi 2p_O)^2 \right.$$

$$\left. (\pi 2p_N)^2,\ {}^1\Sigma^+ \right] + e^-$$

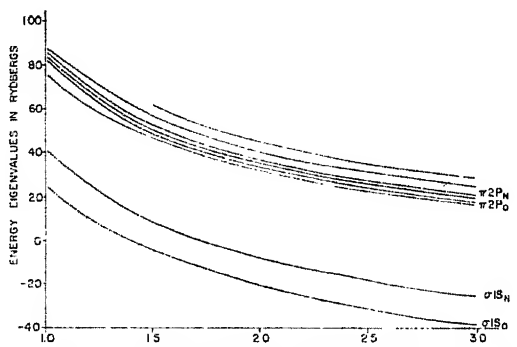
$$\longrightarrow NO^* \left[(\sigma 1s_O)^2 (\sigma 1s_N)^2 (\sigma 2s_O)^2 (\sigma 2s_N)^2 (\sigma 2p_O) (\sigma 2p_N) (\pi 2p_O)^3 \right.$$

$$\left. (\pi 2p_N)^2,\ B^2\pi \right]$$

$$\longrightarrow N\,[1s^2\,2s^2\,2p^3,\ ^2D] + O\,[1s^2\,2s^2\,2p^4,\ ^3P] \qquad (107)$$

Discussion of Previous Work :

Now since the energy eigenvalues resulting from a variational calculation are always *higher* than the true values, it is not possible for an l electron of $N^{+7} - O^{+8} - e^-$ to have an energy such that the energy of "NO" is nearly the same as the energy of NO^+ for any internuclear distance near the equilibrium point.[7] In fact, on the basis of this calculation, the energy difference of "NO" and NO^+ with a zero-energy electron is in the neighborhood of 22 Rydbergs near the equilibrium distance. This energy difference is not surprising when one considers that it represents the energy of interaction between one electron and the fourteen others in a molecule. One must not expect therefore that the potential energy curves of

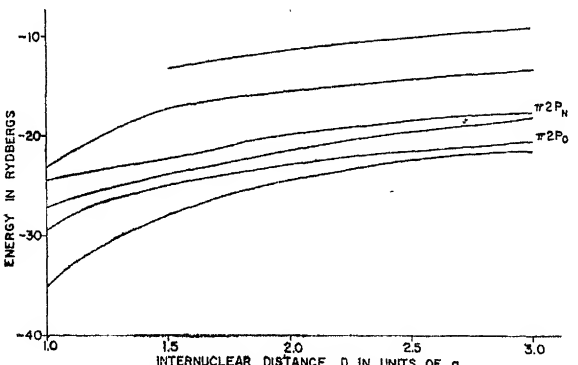


ENERGY EIGENVALUES OF THE THREE BODY SYSTEM N^{+7}-O^{+8}-e^- AS A FUNCTION OF INTERNUCLEAR DISTANCE

FIGURE 2

"NO" will intersect those of the real NO^+. This writer believes that the occurrence of such an intersection in the case of hydrogen[7] is due primarily to the low

interaction energy between the two electrons of a hydrogen atom. The details of the calculation by B and W must now, therefore, be reassessed. In particular, the energy condition for this reaction is



BINDING ENERGY OF A SINGLE ELECTRON ON BARE NITROGEN AND OXYGEN NUCLEI AS A FUNCTION OF THEIR SEPARATION
FIGURE 3

$$E(NO^+) + \frac{\hbar^2 k^2}{2m} = E(NO^*), \tag{108}$$

where the ionic and molecular energies given here are the real energies such as obtained from spectroscopic data.

Calculation of the Transition Matrix Element :

With these ideas in mind, we now proceed to calculate the matrix element for this transition. In the wave functions for this matrix element we must take into account the effects of nuclear vibration as well as electronic motion. It is convenient to regard

$$\psi_a = \Phi_a (r_e R)\, \chi_a (R) \text{ and } \psi_B = \Phi_B (r_e, R)\, \chi_B (R) \tag{109}$$

where the Φ's are functions of the electronic coordinates with the internuclear distance R considered as a parameter, and the χ's are the wave functions representing the nuclear vibration.[13] If we make this substitution in the matrix element in equation (30), we find that

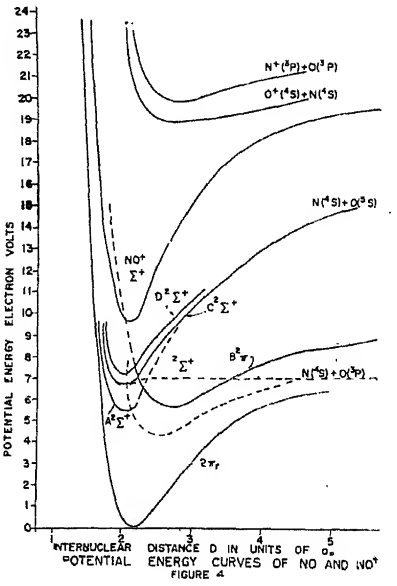
$$\left| \int \psi_a^* H' \psi_B \, d\tau \right|^2 = \left| \int \Phi_a^* H' \Phi_B \, d\tau_e \right|^2 \left| \int \chi_a^* \chi_B \, dR \right|^2 \tag{110}$$

since the perturbation operator H′ is not a function of the internuclear distance.

The Electronic States :

As an approximate wave function for the electronic states B and W used properly asymetrized molecular orbitals, formed from hydrogen-like wave functions, and a plane wave for the free electron. Similarly, we might take hydrogen-like

orbitals for the non-bonding electrons, molecular orbitals formed from hydrogen-like functions for the electrons participating in the bonding, and a plane wave for the free



electron. Even if we accept the plane wave as a good approximation, it is clear that for as many as fifteen electrons this type of wave function is at best only a rough approximation. In addition, the multiplicity of integrals arising from the non-orthogonality of the single-electron wave functions makes a calculation using such a wave function appear quite formidable. Consequently it does not appear desirable to make a calculation in this manner.

Instead it is proposed to make a somewhat rougher, but considerably simpler approximation by making the replacements

$$\Phi_C \longrightarrow \sqrt{\frac{V'}{V}}\, e^{ikr} \longrightarrow \sqrt{\frac{V'}{V}}\, \Phi_B \qquad (111)$$

where V' is the approximate geometrical volume of the molecule. The first replacement here not only removes the difficulty of coulomb enhancement, but as an incident plane wave it denies the existence of any charge at all. It would thus be expected to overcorrect for coulomb enhancement and thus reduce the value of the calculated cross section. The second replacement denies any structure to the wave function Φ_B, an approximation which would be expected to be correct within an order of magnitude since at worst Φ_B has only a few oscillations for any electron.

In particular, the electron just incident is expected to be a $\pi 2p$ electron. If we make this replacement in the electronic integral of equation (110),

$$\left| \int \Phi_C^{*}{}_{H'}\, \Phi_B\, d\tau \right|^2 \longrightarrow \frac{V'}{V} \left| \int \Phi_B^{*}{}_{H'}\, \Phi_B\, d\tau \right|^2 \qquad (112)$$

we can see that the effect of this second replacement is also to lower the value of the calculated cross section. This is so because for low energies the wave length of a free electron is much larger than the size of a molecule; hence by replacing this function by an oscillating function we would expect to lower the value of the integral, and consequently of the matrix element in equation (30).

To obtain a value for the integral on the right of (112) we consider a particular case of equation (31),

$$E(\text{“NO”}, B^2\pi) = E(NO^*, B'\Sigma) + E(N^{+7} - O^{+8} - e^-, \pi 2p) - \frac{56e^2}{R} \tag{113}$$

together with the energy condition for this reaction, extended on the right by again neglecting some of the exchange integrals

$$E(NO^+,{}'\Sigma) + \frac{\hbar^2k^2}{2m} = E(NO,B^2\pi) = E(\text{“NO”},B^2\pi) + \langle \Phi_{NO,B^2\pi} \mid H' \mid \Phi_{NO,B^2\pi} \rangle \tag{114}$$

From these two equations we are able to obtain the result that

$$\langle \Phi_{NO,B^2\pi} \mid H' \mid \Phi_{NO,B^2\pi} \rangle = \left[E(NO,B^2\pi) - E(NO^+,B'\Sigma) \right] - \left[E(N^{+7} - O^{+8} - e^-,\pi 2p) - \frac{56e^2}{R} \right] \tag{115}$$

The value of the first bracket on the right represents the ionization energy of the $B^2\pi$ state of NO, and may be obtained directly from the results of spectroscopic data. The second bracket is simply the quantity E′ plotted in Figure 3.

The Vibrational States :

We consider NO^+ to be initially in its ground state, so that for its vibrational wave function we may take the ground state of a harmonic oscillator :

$$\chi_e(R) = \left[\frac{\alpha^2}{\pi} \right]^{1/4} e^{-\frac{\alpha^2}{2}(R - R_e)^2} \tag{116}$$

where

$$\alpha^2 = \frac{M\omega}{\hbar} \tag{117}$$

M is the reduced nuclear mass, and R_e is the equilibrium position. This is a quite reasonable approximation since the energy of the first excited vibrational state is about 0·3 ev. above the ground state energy.

For the nuclear wave function of the upper state we need the solution to the problem of these atomic interaction in a continuum energy state. However, this solution would be of interest only near the classical turning point. An approximation to the overlap integral of these two states may be made by considering the

Heisenberg uncertainty principle. The lifetime of the upper state would be expected to be of order

$$\tau = -\tau = \lim_{\tau \to 0} \frac{R}{V} \tag{118}$$

where V is the velocity at nuclear separation R. Hence the uncertainty in the energy of the upper state is of order

$$\triangle E \sim \frac{\hbar}{\tau} \tag{119}$$

and the half width of this state, in terms of internuclear distance, is therefore approximately

$$= W \triangle E, \qquad \text{where} \qquad W = -\frac{\partial R}{\partial E}. \tag{120}$$

The overlap integral may therefore be expressed approximately as

$$\int \chi_C^* \chi_B \, dR \cong \frac{W\hbar}{\lambda\tau} \tag{121}$$

where λ is the half width of the harmonic oscillator function.

Numerical Values and Sample Calculations :

The result of the previous sections may be summarized by substituting equations (110), (112) and (121) into equation (30), and obtaining

$$\sigma_C = \frac{6\pi m_e^2 V' (2S+1)}{k^3 \hbar^4} \left| < \Phi_{NO,\, B^2\pi} \left| H' \right| \Phi_{NO,\, B^2\pi} > \right|^2 \left| \frac{W\hbar}{\lambda\tau} \right|^2 \tag{122}$$

For the eigenvalue of the $\pi 2p$ electron in the $n^{+7} - O^{+8} - e^-$ system we obtained the value 33·16 Rydbergs at the internuclear distance D = 2. The nuclear-nuclear repulsion is 56·00 Rydbergs and the ionization energy of the $B^2\pi$ state of NO^+ is about 13·9 ev. or 1·02 Rydbergs. The value in Rydbergs of equation (115) in the neighborhood of the equilibrium position is closely approximated by

$$< \Phi \mid H' \mid \Phi > = 21{\cdot}82 + 3{\cdot}55\,(2.\,O - D) \tag{123}$$

The equilibrium position R_e for the ground state of NO^+ is estimated from the potential energy curve in Figure 4 as 1·125 Å. For equation (117) we estimate also from this curve that

$$\alpha^2 = \frac{M}{\hbar}\omega = \frac{M}{\hbar}\sqrt{\frac{K}{M}} = \frac{\sqrt{MK}}{\hbar} \tag{124}$$

where

$$K = \frac{2 \triangle E}{(\triangle x)^2} = \frac{2(0{\cdot}124 \text{ ev.})}{(0{\cdot}125 \text{Å})^2} = 2{\cdot}54 \times 10^6 \frac{\text{ergs}}{cm^2} \tag{125}$$

so that

$$a^2 = 3{\cdot}76 \times 10^{18}\ \text{cm}^{-2} \tag{126}$$

and the half-width

$$\lambda = 8{\cdot}6 \times 10^{-10}\ \text{cm}. \tag{127}$$

We take for R_C, the intersection of the potential energy curves for the two real states, 1·07 Å. The energy difference between these curves is then approximated by

$$E = 5{\cdot}14\ \text{ev/Å}\ (1{\cdot}07\ \text{Å} - R) \tag{128}$$

so that the value of W in equation (120) is

$$W = 121\ \text{cm/erg} \tag{129}$$

and the internuclear distance corresponding to a Franck-Condon transition at 1 ev. is

$$R_k = 1{\cdot}051\ \text{Å} \tag{130}$$

The life-time τ of the upper state in equation (118) is of order

$$\tau \sim 3{\cdot}4 \times 10^{-14}\ \text{sec}. \tag{131}$$

so that the value of the overlap integral (121) is

$$\int \chi_C\, {}^*\chi_B\, dR \cong \frac{W\hbar}{\lambda\tau} = 4{\cdot}4 \times 10^{-3} \tag{132}$$

For the geometrical volume of the NO molecule we estimate

$$V' = \frac{4}{3}\pi a_0^3 + (1{\cdot}07\ \text{Å})\ \pi a_0^2 \cong 1{\cdot}5 \times 10^{-24}\text{cm}.^3 \tag{133}$$

The multiplicity of the bound state is 2, so the coefficient

$$\frac{6\pi m_e V'(2S+1)}{k^3\hbar^4} = \frac{6\pi m_e^{\frac{3}{2}} V'\,(2)}{2\sqrt{2}\,\hbar E^{3/2}} = 5{\cdot}72\ \text{cm}^3\text{gm}^{\frac{1}{2}}\text{erg}^{-1}\ \text{sec}^{-1}/E^{3/2} \tag{134}$$

For an energy of 1 ev. we thus obtain

$$\sigma_C = 12 \times 10^{-16}\ \text{cm}^2 \tag{135}$$

by substituting (123), (132), and (134) into equation (122).

V. RESULTS AND DISCUSSION

Discussion of Numerical Result :

We obtained in this calculation for the dissoci ative recombination cross section of NO^+ for electrons of energy 1 ev. the value

$$\sigma_c = 12 \times 10^{-16} \text{ cm.}^2$$

It is difficult to estimate the accuracy of this result. In particular, it is inversely proportional to the square of the lifetime of the upper state, for which we made only the classical estimate. It also varies as the square of the transition matrix element, whose value is subject to appreciable error, not only from the manner in which it was approximated, but also from the value of the normalization volume for the free electron which was estimated from geometrical considerations. In their recent paper Nicolet and Aikin[5] used a value of about 3×10^{-16} cm.^{2} for thermal electrons in the ionosphere. The value calculated here is rather higher than this estimate, agreeing more nearly with that of O_2 and N_2. As might be expected, the cross section is of the order usually expected for gas-kinetic reactions.

A Difficulty with Present Calculation for Ionospheric Parameters :

Of particular difficulty in theoretical calculations for ionospheric parameters based on molecular physics is the low energy of thermal electrons ($\sim$ ·04 ev.). This arises from the use of first-order perturbation theory or Born approximations as the only reasonable and available method. No attempt has been made in this work to surmount this difficulty, and the extension of this method into higher order theory would present a quite formidable problem at this time. However, this problem involves no more than 15 electrons, and there is every reason to believe that with the use of future high-speed electronic computers an effectively exact solution could be found, but not easily nor cheaply.[14]

Theoretical Considerations :

The theory for the calculation of cross sections for dissociative recombination is by no means well-developed and ordered. Many approximations have been made in this work, at least two of which seem a bit severe, namely: the value of the matrix element and the nuclear wave function for the upper state in the neighborhood of the classical turning point. Such approximations can be justified only on the basis of getting a very rough answer. Indeed, even a rough answer may be of some significance to researchers in ionosphere physics. In this work the writer has concentrated mainly in improving the techniques for this type of calculation. Probably the most profitable exercise for the near future would be an analogous calculation for oxygen and nitrogen. These cases involve approximately the same number of electrons, and their values are reasonably well known from experiment.[14] Finally, the writer suspects that an accurate calculation will very likely involve the theory of exchange collisions.

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Appendix A

LIST OF SYMBOLS

Symbol	Pages	Description
a_0	587, 589	Radius of Bohr orbit, 0·529 Å.
a	590	Semi-internuclear distance, see equation (52).
A		A subscript denoting one of the nucleii.
B		A subscript denoting the nucleus not designated by A.
B and W		Bauer and Wu, reference 7.
D	590	Internuclear distance, see equation (50).
e^-		An electron.
E		Energy of the incident electron.
E_n	581, 588	The eigenvalues of the problem.
h		Planck's constant, $6{\cdot}63 \times 10^{-27}$ erg-sec.
$\hbar$		Planck's constant divided by 2π, $1{\cdot}054 \times 10^{-27}$ erg-sec.
H′, H″	580	Free hydrogen atoms.
H_2^+	580	A positively charged hydrogen molecule-ion.
J_a	592	Interaction integral, see equation (71).
k	585,586	Propagation number of incident electron.

Symbol	Pages	Description
$\vec{k}$	585	Propagation vector of incident electron.
$K_{a\gamma}$	597	Interaction integral, see equation (93).
$K_{\alpha\beta}$	593	Interaction integral, see equation (99).
m_e		Mass of an electron, $9{\cdot}11 \times 10^{-28}$ gm.
N^{+7}		A bare nitrogen nucleus.
"NO"		A fictitious nitric oxide molecule.
O, O′, O″		Free Oxygen atoms.
O^{+8}		A bare oxygen nucleus.
R_{AB}		Internuclear distance.
R_e	605	Equilibrium internuclear distance.
u_n		A complete, but arbitrary, set of orthonormal functions.
V	585	Normalization volume of incident eleetron wave function.
V′	604	Geometrical volume of NO molecule.
W_α		Eigenvalue of hydrogen wave function.
Z		Atomic number.
δ_{nj}		The Kronecker δ – function : $\delta_{nj} = 0$ if $n \neq j$, and $\delta_{nj} = 1$ if $n = j$.
λ		Molecular orbital quantum number, or, according to context.
λ	606, 607	Halfwidth of harmonic oscillator function.
μ		A confocal elliptical coordinate.
ν		A confocal elliptical coordinate.
π	602	Molecular orbital with $\lambda = 1$.
$\rho_{(E)}$	583, 585	Density of states.
σ_α , σ_β	588, 590	A radial parameter, see equation (37) and (60).
σ		Molecular orbital with $\lambda = 0$
σ_c		Cross section for electron capture.
τ	606, 607	Lifetime of upper state.
Φ_B , Φ_C	603	Electronic wave functions, see equation (109).
χ	537, 593	Hydrogenic wave function.
χ_B , χ_C	603	Nuclear vibrational wave function, see equation (109).
ψ	581	A quantum mechanical wave function.
ψ_B , ψ_C	584	Particular wave functions described in detail.

INELASTIC COLLISIONS BETWEEN ATOMIC SYSTEMS

By

D. R. BATES

Department of Applied Mathematics, The Queen's University of Belfast, Northern Ireland

ABSTRACT

An account is presented of the semiclassical (impact parameter) theory of collisions between atomic systems. Stress is laid on the importance in some cases of coupling between excited states. This is discussed from the viewpoint of the third-order approximation to the solution of the set of differential equations describing a collision.

In the theoretical treatment of the excitation or ionization of an atomic system in an encounter with another atomic system it is permissible to regard the nuclei as classical particles. Unless the energy of relative motion is very low it is, indeed, permissible to regard the nuclei as *classical particles of infinite mass*. This may be done even if Coulomb forces are involved. Bates and Boyd (1962) have for example, shown that the fractional error made in calculating the first Born approximation to the cross section of

$$He^+(1s) + He^{2+} \rightarrow He^+(2s) + He^{3+} \tag{1}$$

is only 0·3 per cent at the maximum of the cross section curve.

1. GENERAL EQUATIONS

Let a target atomic system A be located at the origin of a fixed coordinate system and let a projectile nucleus B move with constant speed v along a line parallel to and at a distance ρ from the Z axis. Denote the Hamiltonian operator associated with A by H and denote the eigenfunctions and corresponding eigenenergies by $\phi_n(\mathbf{r})$ and ε_n so that

$$H\,\phi_n(\mathbf{r}) = \varepsilon_n\,\phi_n(\mathbf{r}). \tag{2}$$

If the interaction potential due to the presence of B with position vector $\mathbf{R}$ is $V(\mathbf{r}, \mathbf{R})$ the complete electronic wave function $X(\mathbf{r}, t)$ satisfies the time-dependent Schrödinger equation

$$\left\{ H + V(\mathbf{r}, \mathbf{R}) \right\} X(\mathbf{r}, t) = i\hbar \frac{\partial X(\mathbf{r}, t)}{\partial t} \tag{3}$$

It is convenient to express $X(\mathbf{r}, t)$ in the form

$$X(\mathbf{r}, t) = \sum_n a_n(Z)\,\phi_n(\mathbf{r})\,exp\left\{\frac{-i\,\varepsilon_n\,t}{\hbar}\right\} \tag{4}$$

reminders of the dependence of the expansion coefficients $a_n(Z)$ on the impact parameter ρ and azimuthal angle Φ of the path of B being omitted for brevity. Choosing the origin of time so that

$$Z = v\,t \tag{5}$$

substituting (4) in (3) and using (2), it may be seen that

$$i\hbar v \sum_n \frac{\partial a_n(Z)}{\partial Z} \phi_n(r) \exp\left\{\frac{-i\varepsilon_n Z}{\hbar v}\right\} = V(\mathbf{r},\mathbf{R}) \sum_n a_n(Z)\phi_n(r) \exp\left\{\frac{-i\varepsilon_n Z}{\hbar v}\right\} \quad (6)$$

and hence that

$$i\hbar \frac{\partial a_q(Z)}{\partial Z} = 1/v \sum_n a_n(Z)\, v_{qn}(\mathbf{R}) \exp\left[\frac{-i}{\hbar v}(\varepsilon_n - \varepsilon_q) Z\right] \quad (7)$$

where

$$v_{qn}(\mathbf{R}) = \int \phi_q^*(\mathbf{r})\, V(\mathbf{r},\mathbf{R})\, \phi_n(\mathbf{r})\, d^3\mathbf{r}. \quad (8)$$

If A is initially in state p equations (7) must be solved subject to the boundary conditions

$$a_n(-\infty) = \delta_{pn} \quad (9)$$

δ_{pn} being the Kronecker delta function. The probability that state q is occupied finally is

$$P_{pq} = |a_q(\infty)|^2 \quad (10)$$

and the $p \to q$ collision cross section is

$$Q_{pq} = \int_0^{2\pi} \int_0^{\infty} \rho P_{pq}\, d\rho\, d\rho. \quad (11)$$

2. FIRST BORN AND DISTORTION APPROXIMATIONS

It is apparent from (9) that a zero-order approximation to the required solution is

$$a_n(Z) = \delta_{pn}. \quad (12)$$

Substitution in (7) gives

$$a_q(Z) = \delta_{pq} - \frac{i}{(\hbar v)} \int_{-\infty}^{Z} v_{qp}(\mathbf{R}) \exp\left[\frac{-i}{\hbar v}(\varepsilon_p - \varepsilon_q) Z\right] dZ. \quad (13)$$

Using (10) and (11) the cross section Q_{pq} may now be calculated. This is the impact parameter version of the *first Born approximation*. The wave version yields a simpler formula because resolution into partial waves may here be avoided (cf. Mott and Massey 1949). In general the wave version of an approximation is more complicated than the impact parameter version.

The terms on the right of (7) which involve the diagonal matrix elements are of special importance since they are secular in the sense that they do not contain an oscillatory exponential function.* Proper account of them is taken

* Terms involving matrix elements connecting states of equal energy also have this characteristic.

in what is called *the distortion approximation*. This may readily be derived. Introducing a new set of coefficients defined according to

$$c_n(Z) = a_n(Z)\, exp\left[\frac{i}{\hbar v}\int_0^Z v_{nn}(\mathbf{R})\, dZ\right] \tag{14}$$

(7) becomes

$$i\hbar\frac{\partial c_q(Z)}{\partial Z} = 1/v \sum_{n\neq q} c_n(Z)\, v_{qn}(\mathbf{R})\, exp\left[\frac{-i}{\hbar v}\int_0^Z \delta_{nq}(\mathbf{R})\, dZ\right] \tag{15}$$

with

$$\delta_{nq}(R) = v_{nn}(\mathbf{R}) + \varepsilon_n - v_{qq}(\mathbf{R}) - \varepsilon_q. \tag{16}$$

The unwanted secular terms no longer occur. Taking the zero order approximation to be

$$c_n(Z) = \delta_{pn} \tag{17}$$

and substituting on the right of (15) it is seen that on the corresponding first order approximation

$$P_{pq} = |\, c_q(\infty)\,|^2$$

$$= \frac{1}{(\hbar v)^2}\left|\int_{-\infty}^{\infty} v_{qp}(\mathbf{R})\, exp\left[\frac{-i}{\hbar v}\int_0^Z \delta_{pq}(\mathbf{R})\, dZ\right] dZ\right|^2. \tag{18}$$

The first Born and distortion approximations have been applied to the following collision processes :

$$H(1s) + H^+ \text{ (or } He^{2+}) \rightarrow H(2s) + H^+ \text{ (or } He^{2+}) \tag{19}$$

(Bates 1959) ;

$$H(1s) + H^+ \text{ (or } He^{2+}) \longrightarrow H(2p) + H^+ \text{ (or } He^{2+}) \tag{20}$$

(Bates 1961) ;

$$He(1s^2\ {}^1S) + H^+ \text{ (or } He^{2+}) \rightarrow He(1s, 2p \text{ or } 3p\ {}^1P) + H^+ \text{ (or } He^{2+}) \tag{21}$$

(Bell 1961)

and

$$Na(3s\ {}^2S) + H^+ \rightarrow Na(3p\ {}^2P) + H^+ \tag{22}$$

(Bell and Skinner 1962). Though the distortion approximation makes allowance for more matrix elements than the first Born approximation, it yields less accurate results in some instances.

3. COUPLING APPROXIMATIONS

The first Born and distortion approximations are not unduly difficult to evaluate since each involves only an *isolated* first order differential equation. *Coupled* equations arise if full account is taken of matrix elements other than the

one connecting the initial state to the final state and those which are diagonal. For example, the inclusion of the matrix element joining the final state to the initial state (*back-coupling*) leads to

$$\left.\begin{aligned} i\hbar\,\frac{\partial c_q(Z)}{\partial Z} &= 1/v\; c_p\,(Z)\; v_{qp}\,(R)\; exp\left[\frac{-i}{\hbar v}\int_0^Z \aleph_{pq}\,(\mathbf{R})\; dZ\right] \\ i\hbar\,\frac{\partial c_p\,(Z)}{\partial Z} &= 1/v\; c_q(Z)\; v_{pq}\,(R)\; exp\left[\frac{-i}{\hbar v}\int_0^Z \aleph_{qp}\,(\mathbf{R})\; dZ\right] \end{aligned}\right\} \qquad (23)$$

Such coupled equations are awkward but fortunately the development of high-speed electronic computers has made the solution of them practicable.

Skinner (1962) has treated process (20) taking into account the direct transition matrix elements $(2p_x, 1s)$ and $(2p_z, 1s)$; the diagonal matrix elements $(1s,1s)$ $(2p_x, 2p_x)$ and $(2p_z, 2p_z)$; and the rotation-coupling matrix elements $(2p_x, 2p_z)$ and $(2p_z, 2p_x)$ connecting the degenerate states of the $2p$ level. In collaboration with Bell he later included, in addition, the back-coupling matrix elements $(1s, 2p_x)$ and $(1s, 2p_z)$ thus making full allowance for all matrix elements involving only the initial or final states. Some of the results are displayed in table 1. It is seen that

TABLE 1

Calculated results on $H(1s) + H^+ \longrightarrow H(2p) + H^+$ collisions.

Matrix elements*

Log of energy of incident proton in kev	+Direct transition[1] $(2p_x,1s)+(2p_z,1s)$	+ Distortion[1] $(1s, 1s)+(2p_x, 2p_x)+(2p_z, 2p_z)$	+Rotation-coupling[2] $(2p_x, 2p_z)+(2p_z,2p_x)$	+Back-coupling[3] $(1s, 2p_x)+(1s, 2p_z)$
	Cross section in units of $\pi\ a_0^2$ $(8{\cdot}8\times10^{-17}\ cm^2)$			
1·00	1·722	0·561	0·640	0·549
1·25	1·891	1·201	1·343	1·233
1·50	1·755	1·559	1·663	1·589
1·75	1·435	1·446	1·528	1·487
2·00	1·091	1·135	1·184	1·168
2·25	0·781	0·817	0·840	0·834
2·50	0·535	0·554	0·566	0·564

distortion is more important than the two types of coupling considered. Bell and Skinner (1962) have also carried out similar calculations on process (22) which has

*The matrix elements included are those at the head of the column concerned together with those at the heads of all columns to the left.

[1]Bates (1961) [2]Skinner (1962) [3]Bell and Skinner (1962)

a very high transition strength. They find that back-coupling is here of major importance. The results obtained when it is ignored are absurd in that the calculated probability of excitation then exceeds unity over a wide range of impact parameters and velocities.

It has long been realized that the inclusion of back-coupling ensures that the calculated probability is less than unity. Since this is an obvious requirement there has been a tendency to assume that back-couplingis the dominant coupling. The assumption is not always correct. Coupling between the final excited state and other excited states or the continuum, may be more important.

Some insight into the position may be gained by solving (15) by successive approximations. It is convenient to write

$$I_{rs}(Z) \simeq (1-\delta_{sr})\, v_{sr}(R) \exp\left[\frac{-i}{\hbar v}\int_{0}^{Z} \aleph_{sr}(R)\, dZ\right] \qquad (24)^*$$

(in which the order of the subscripts on the left has been changed from the conventional order on the right to bring it into harmony with the associated $r \to s$ virtual transition) ; and to write

$$g_{rs}(Z) = \int_{-\infty}^{Z} I_{rs}(Z)\, dZ \qquad (25)^*$$

Elementary analysis yields

$$\begin{aligned} c_q(\infty) = \delta_{pq} &- \frac{i}{(\hbar v)} g_{pq}(\infty) \\ &- \frac{1}{(\hbar v)^2} \sum_n \int_{-\infty}^{\infty} g_{pn}(Z)\, I_{nq}(Z)\, dZ \\ &- \frac{i}{(\hbar v)^3} \sum_n \sum_m \int_{-\infty}^{\infty} \left\{ \int_{-\infty}^{Z} g_{pm}(Z)\, I_{mn}(Z)\, dZ \right\} I_{nq}(Z)\, dZ, \end{aligned} \qquad (26)$$

The leading term contributing to back-coupling is

$$B = \frac{-i}{(\hbar v)^3} \int_{-\infty}^{\infty} \left\{ \int_{-\infty}^{Z} g_{pq}(Z)\, I_{qp}(Z)\, dZ \right\} I_{pq}(Z)\, dZ. \qquad (27)$$

It comes from the $p \to q \to p \to q$ sequence of virtual transitions and is important if the $p \to q$ transition is strong. However, there may well be an excited state n such that the sequence $p \to q \to n \to q$ is even more important. This sequence gives rise to a term

$$X = \frac{-i}{(\hbar v)^3} \int_{-\infty}^{\infty} \left\{ \int_{-\infty}^{Z} g_{pq}(Z)\, I_{qn}(Z)\, dZ \right\} I_{nq}(Z)\, dZ. \qquad (28)$$

*As need scarcely be said I_{rs} and g_{rs} are functions of ρ and ϕ as well as of the displayed variable Z.

Some indication of the relative magnitudes of B and X may be obtained from the line strengths of the transitions concerned (though it must be remembered that the interpretation is complicated by the oscillatory exponential functions occurring in the integrals involved). Table 2 gives some relevant information on line strengths

TABLE 2

Information relating to coupling

Atom	Transition	Line strength[1] (atomic units)
Hydrogen	$1s-2p$	3·32
	$2p-2s$	54·0
	$2p-3d$	90·0
Sodium	$3s-3p$	38
	$3p-4s$	37
	$3p-3d$	132

of hydrogen and sodium. It is seen that the line strength of the transition connecting the ground state to the first excited state is not as strong as the line strength of transitions connecting the first excited state to other excited states.

Since the effect of back-coupling is inappreciable for the H ($1s-2p$) transition it is unlikely that any three-step sequence influences the cross section to a major extent in this case.

The position regarding the Na ($3s-3p$) transition is different. Back coupling is here important. In view of this it would seem (cf. table 2) that coupling to the $4s$ and $3d$ states (and through them to other excited states) should also be taken into account. If this is not done the cross section obtained is likely to be closer to that for all inelastic $H^+-Na(3s)$ collisions than to that for the particular process under consideration. Measurements are needed on the cross sections for excitation to the higher levels and for ionization.

ACKNOWLEDGMENT

This work was supported by the U. S. Office of Naval Research under Contract N 62558-2637.

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THEORY OF SECONDARY ELECTRON EMISSION FROM METAL SURFACE BY HIGH ENERGY ION AND ATOM BOMBARDMENTS

By

S. P. KHARE *and* S. N. GHOSH

J. K. Institute of Applied Physics, University of Allahabad, Allahabad

[Received on 30th March, 1963]

ABSTRACT

Theory for kinetic ejection of secondary electrons from solid surfaces by bombardments of positive ions and neutral atoms as proposed by authors are reviewed after considering that the ionization process is responsible for such ejection.

Theoretical and experimental results for secondary electron emission coefficient, γ_e for aluminium bombarded by H^+, H^0, He^+, He^0 and N_2^+ for energies greater than 25 keV are presented. The calculated ratio of $\gamma_{H^0}/\gamma_{H^+}$ and $\gamma_{He^0}/\gamma_{He^+}$ are compared with exprimental results.

I. INTRODUCTION

The problem of secondary electron emission from metal surfaces by ion and neutral atom bombardments resolves into two secondary problems: (1) production of internal secondaries (2) escape of internal secondaries from the metal surface. When a metal surface is bombarded by an ion, it interacts with atoms and weakly-bound electrons of the metal leading to the production of excited electrons inside the metal (internal secondaries). The theoretical calculation of Dalgarno and Griffing[1] for ions passing through hydrogen atoms show that in the high-energy range, ionization is the most important process. Based upon this calculation. It is assumed that the internal secondaries are produced by ionization of metal atoms.[2]

We shall consider an incident H^+ ion which has penetrated through a depth x inside the metal. If v denotes the velocity of the incident ion at this instant and Q_{nl}, the ionization cross-section for nl shell of the metal atom for this velocity, the internal secondaries produced between depths x and $x + dx$ per unit area is given by

$$d\gamma_i = N \sum_{nl} Q_{nl}\, dx \qquad \ldots (1)$$

where N is the number of metal atoms per c. c. The summation extends over all shells of the atom. Assuming that the incident ion can ionize metal atoms till it has penetrated through a depth L, we have,

$$\gamma_i = N \int_0^L \sum_{nl} Q_{nl}\, dx$$

Expressing in terms of the kinetic energy T of the incident ion,

we have

$$\gamma_i = N \int_{T_0}^{T_1} \frac{\sum_{nl} Q_{nl}}{dT/dx} \cdot dT$$

where T_o is the initial energy of the ion and T_I the minimum energy required for ionization of the metal atom.

It may be noted that the internal secondaries if produced below a strip, called the *productive strip*, will be heavily absorbed and will be unable to reach the surface of the metal. Assuming Bethe's expression for stopping power, it can be shown that the energy loss of the incident ion in the productive strip is very small in comparison with the initial energy of the ion. Hence Q_{nl} can be placed outside the sign of integration, one then obtains

$$\gamma_i = N \sum_{nl} Q_{nl} \int_0^L dx.$$

Hence the total number of secondaries is given by

$$\gamma_i = N \sum_{nl} Q_{nl}. L.$$

If the incident beam instead of penetrating normal to the surface makes an angle θ with the normal, L is replaced by L Sec θ and we have

$$\gamma_i (\theta) = N \sum_{nl} Q_{nl} L \text{ Sec } \theta = \gamma_i \text{ (o) Sec } \theta, \qquad \ldots (2)$$

where γ_i (o) denotes the internal secondaries produced by normally incident ions. The above equation shows that the variation of γ_i follows a sec law.

We shall now consider the probability of escape of internal secondaries produced at a depth x. These secondaries while moving towards the surface, lose energy on colliding with other particles. In the absence of theoretical expression for the absorption of the electrons inside the metal, an exponential law is assumed by the authers[2] namely that if the number of secondaries produced at a depth x is F (x) then only F (x) $e^{-\alpha x}$ electrons are able to reach the surface where α is the absorption coefficient.

With regard to the probability that an electron after reaching the surface from the interior may be able to escape from the metal, it should be noted that the electron should overcome the inner work function and the surface dipole potential. The inner work function can be neglected, because the time taken by secondaries to move to the surface is small compared with the relaxation time of the conduction electron. As regards the surface dipole potential, Sternglass[3] has shown that for isotropic distribution, the escape probability is 0·5.

According to Bethe[4]

$$Q_{nl} = \frac{2\pi z_i^2 e^4 c_{nl} Z_{nl}}{mv^2 | E_{nl} |} . ln \left(\frac{2mv^2}{c_{nl}} \right) \qquad \ldots (3)$$

where

z_i —charge of the ion

E_{nl}—ionization potential of the nl shell

Z_{nl}—number of electrons in the *nl* shell

C_{nl}—certain mean of $E_k - E_{nl}$ having a value of the same order as E_{nl}

and $c_{nl} = \frac{Z_e q^2}{n^2 a_0^2} \int |X_{nl}, k|^2 \, dk$; its value ranges between ·05 and 0·3.

Substituting the value of Q_{nl} in Eqn. (1) and replacing v by T and mass (M) of the incident ion, one obtains

$$\gamma_e = \frac{0{\cdot}25\ N}{a} \frac{\pi z_i^2 \varepsilon^4 M}{mT} \sum_{nl} \frac{c_{nl}}{|E_{nl}|} ln \left(\frac{\frac{4m}{M} T}{c_{nl}} \right) \quad \ldots (4)$$

As the value of α is not known accurately, it is determined by coinciding the calculated value of γ_{H^+} for 1 Mev for H_1^+ - Al mission with the observed value. The value of c_{nl} is obtained from Bethe's table and c_{nl} is assumed to be 1/10 of E_{nl}.

In table I the variation of γ_{H^+} calculated from formula (4) with the energy of the ions are shown for aluminium target bombarded by H^+ and D^+. Values observed experimentally for Al target bombarded by H^+ by Hill *et al*[5] and Agrset *et al*[6] and for Cu bombarded by D^+ obtained by Akishin[7] are also shown for comparision. In Fig. 1 experimental values for H^+ ions are compared with the calculated values.

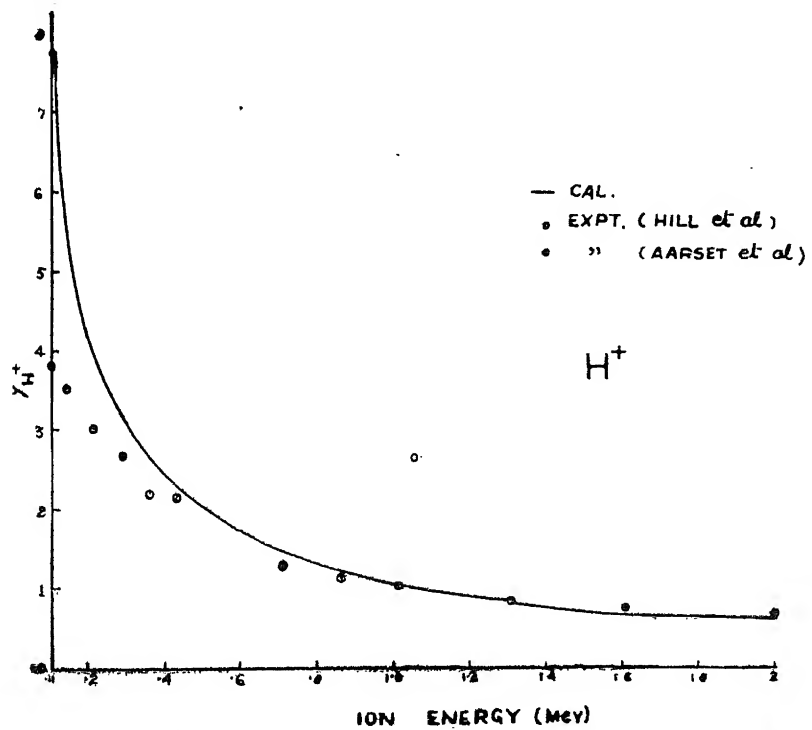

Fig. 1. Comparison of experimental values of γ_e for H^+ ion with the calculated curve. (● : obtained experimentally for Al target by Hill *et al* and ○ by Aarset et al for the same target).

TABLE I

Energy (Mev)	H^+ For Al (Cal)	H^+ For Al (obs)	D^+ For Al (Cal)	D^+ For Cu (obs)
0·7	1·43	1·31	2·64	...
1·0	1·08	1·08	1·92	1·41
2·0	0·59	0·68	1·18	1·06
3·0	0·41	...	0·824	0·85
4·0	0·32	...	0·604	0·71

Considering Fig. 1, we find that compared to the experimental values, calculated values of γ_{H^+} increase more rapidly with the decrease of ionic energy. This is due to the fact that Bethe's formula is correct only in the Mev region and gives higher cross-section in the low energy region. Also Kaila and Saha[8] found that Bethe's formula for stopping power gives higher values than the experimental results in the low energy region. They introduced an empirical multiplying factor so that it may agree with the experimental data upto 25 kev. Similarly Bethe's formula for ionization cross-section is modified and we assume[9]

$$Q_{n1} = \frac{Q_B}{1 + \beta/T}$$

where Q_B is the ionization cross-section obtained from Bethe's formula and β a constant.

Hence we obtain

$$\gamma_{H^+} = \frac{0{\cdot}25\ N\ Q_{H^+}}{\alpha} \qquad \ldots (5)$$

where

$$Q_{H^+} = \frac{\Sigma\ Q_B}{1 + \beta/T}\ .$$

γ_{H^+} for Al at different energies ($T > 200$ Kev) have been calculated from the above equation.

For $T < 200$ Kev, one should consider the importance of charge changing collisions. For proton beam, the capture cross-section σ_{01} is appreciable (10) at low energy and hence some of the protons are converted into neutral hydrogen atoms of same energy travelling in the same direction as the incident proton beam. Therefore, while traversing a target a low energy proton beam should be considered as a *two-component* system consisting of H^+ and H^0, each capable of

producing internal secondaries. Treating the beam as a two-component system, we get (9)

$$\gamma_{H^+} = \gamma'_{H^+} \left\{ R f_{0\infty} \left\{ 1 - \frac{1}{1 + \frac{N}{\alpha}\sigma_{01}\left(1 + \frac{f_{0\infty}}{f_{1\infty}}\right)} \right\} + \left\{ f_{1\infty} + \frac{f_{0\infty}}{1 + \frac{N}{\alpha}\sigma_{01}\left(1 + \frac{f_{0\infty}}{f_{1\infty}}\right)} \right\} \right\} \quad \ldots (6)$$

where γ'_{H^+} = secondary electron emission coefficient where the beam is treated as one-component system

and $R = Q_{H^0}/Q_{H^+}$.

The calculated values of γ_{H^+} for Al obtained from Eqn. (6) are shown in Fig. (2). The experimental values obtained by Cousinié *et al*[11], Hill *et al*[5]

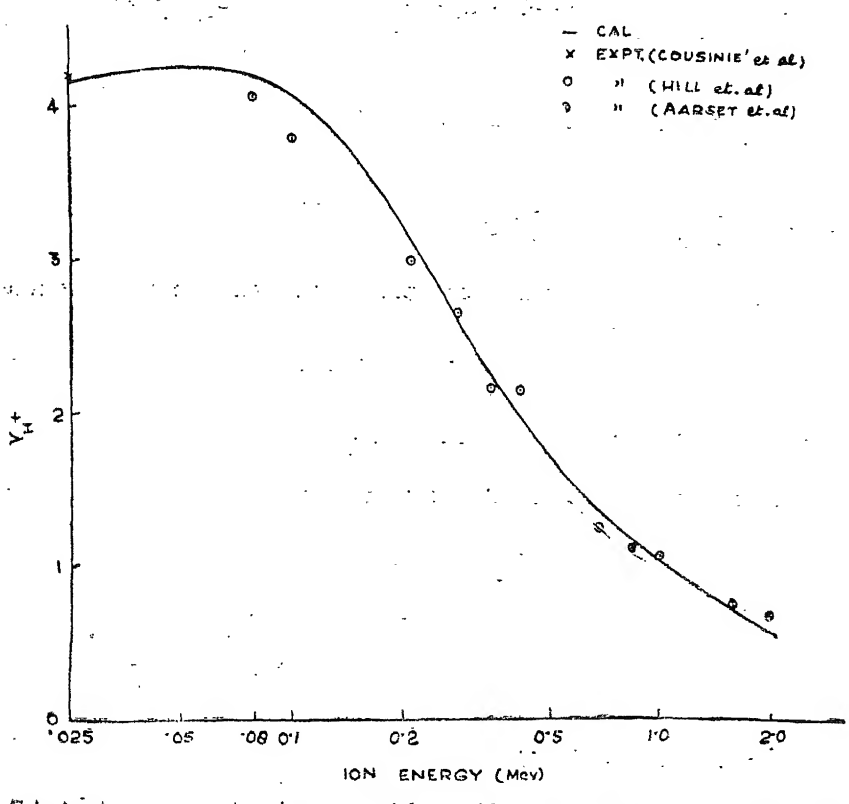

Fig. 2. Calculated variation of γ_{H^+} for aluminium with proton energy is compared with that obtained experimentally.

and Aarset *et al*[5] in the energy ranges 3-30 kev, 78-426 kev and 0·7 – 2 Mev are also shown for comparison. Comparing Figs. (1) and (2), we find that the agreement between the experimental and calculated values is closer in Fig. (2) which is achieved by using modified Bethe's formula for ionization cross-section and treating the beam as a two-component system.

II. SECONDARY ELECTRON EMISSION BY HIGH ENERGY HYDROGEN ATOM BOMBARDMENT ON METALS

Since in the high energy region loss cross-section is many times higher than the capture cross-section (10), hydrogen atom while traversing a target is ionized yielding one proton and an electron. The energy of the proton is the same as that of the hydrogen atoms and the electron energy is $T/(M/m)$, m being mass of the electron.

Thus

$$H^{\circ}(T) \longrightarrow H^{+}(T) + \bar{e}\ (T/(M/m)).$$

A neutral beam of hydrogen atoms is therefore treated inside the target as a *three-component system* consisting of protons, hydrogen atoms and electrons. Each of these three kinds of particles are capable of producing internal secondaries.

Consider now a beam of hydrogen atoms penetrating through a metal. The fractional concentrations of neutral atoms and protons at a depth of x are given by

$$f_{\circ} = \frac{\sigma_{10}}{\sigma_{10}+\sigma_{01}} + \frac{\sigma_{01}}{\sigma_{10}+\sigma_{01}}\, e^{-N(\sigma_{10}+\sigma_{01})x}$$

$$\text{and } f_1 = \frac{\sigma_{01}}{\sigma_{10}+\sigma_{01}} - \frac{\sigma_{01}}{\sigma_{10}+\sigma_{01}}\, e^{-N(\sigma_{10}+\sigma_{01})x}$$

Since each hydrogen atom produces one proton and one electron the number of electrons will also be equal to f_1.

The number of internal secondaries produced between depths x and $x+dx$ is given by

$$d\gamma_i = N f_{\circ} Q_H^{\circ}\, dx + N f_1 Q_H^{+}\, dx + f_1 A dx \qquad \ldots (7)$$

where A represents the number of internal secondaries produced by electrons in traversing through a unit distance.

Proceeding as for proton bombardment we obtain

$$\gamma_{H^{\circ}(T)} = R\gamma'_{H^{+}(T)} \left[f_{\circ\infty} + \frac{f_{1\infty}}{1+\frac{N}{\alpha}\sigma_{01}\left(1+\frac{f_{\circ\infty}}{f_{1\infty}}\right)} \right]$$

$$+ \left[\gamma'_{H^{+}(T)} + \gamma_{\bar{e}(T/1836)} \right] \left[1 - \frac{1}{1+\frac{N}{\alpha}\sigma_{01}\left(1+\frac{f_{\circ\infty}}{f_{1\alpha}}\right)} \right] \qquad \ldots (8)$$

For $T > 200$ kev, we have $\frac{f_{0\infty}}{f_{1\infty}} << 1$ and $f_{1\infty} \simeq 1$ (2) hence we obtain

$$\gamma_{H^\circ}(T) = \frac{\left[\gamma'_{H^+}(T) + \gamma_{\bar{e}}(T/1836)\right]\frac{N}{\alpha}\sigma_{01} + R\,\gamma'_{H^+}(T)}{1 + \frac{N}{\alpha}\sigma_{01}} \quad \ldots (9)$$

$\gamma_{H^\circ}(T)$ is calculated for $T < 200$ kev from Eqn. (8) and for $T > 200$ kev from Eqn. (9). The value of $\gamma_{\bar{e}}(T/1836)$ is obtained from the enpression given by Lye and Dekker (12) after assuming $\gamma_{\bar{e}}\ (max) = 1$ and $T_{max} = 300$ ev, obtained experimentally by Bruining (13). The calculated results are shown in Fig. (3).

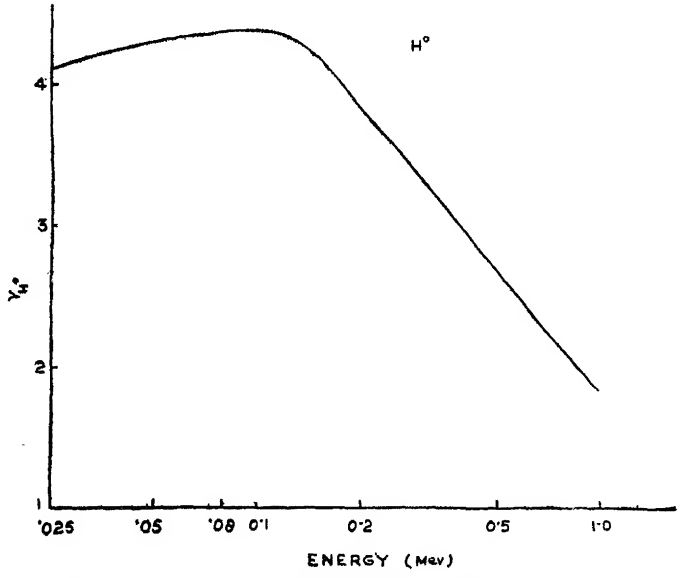

Fig. 3. Variation of γ_{H° for aluminium with energy of the bombarding atom.

The ratio $\gamma_{H^\circ}/\gamma_{H^+}$ is also estimated using the calculated values of γ_{H° and γ_{H^+} obtained before. The results are shown in Figs. (4) and (5). The experi-

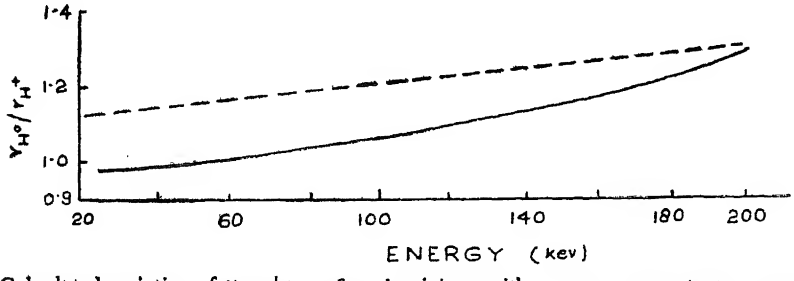

Fig. 4. Calculated variation of $\gamma_{H^\circ}/\gamma_{H^+}$ for aluminium with proton energy (solid curve) is compared with that obtained by Stier et al for brass (dotted curve).

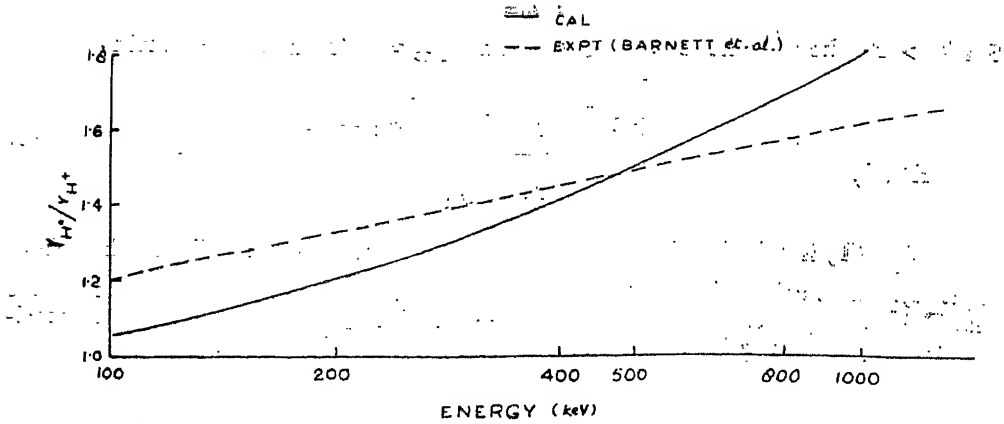

Fig. 5. Calculated variation of $\gamma_{H^o}/\gamma_{H^+}$ for aluminium with proton energy is compared with the experimental values obtained by Barnett et al for brass.

mental values obtained by Stier *et al* (14) and Barnett *et al* (15) for brass in the energy range 20 kev – 1 Mev are also given for comparison.

III. SECONDARY ELECTRON EMISSION BY HELIUM ION AND ATOM BOMBARDMENTS

Let us consider a He^o or He^+ beam penetrating through a metal. At a depth x, the fractions of He^o, He^+ and He^{++} for T > 80 kev are given by

$$f_i = f_{i\infty} + \left[P(z_1\, i)\, e^{Nxq} + N(z_1\, i)\, e^{-Nxq} \right] e^{-N\,x/2\ \Sigma\,\sigma_{it}} \qquad \ldots (10)$$

where

i = 0, 1, 2—charge of the helium components He^o, He^+ and He^{++} respectively.

z = 0 or 1—charge of the initial beam of helium atom or ion

$$q = +\tfrac{1}{2}\left[(g-a)^2 + 4bf \right]^{\frac{1}{2}}, \quad \Sigma\,\sigma_{if} = -(a+g)$$

$$a = -(\sigma_{10} - \sigma_{11} + \sigma_{21}) \quad , \quad f = (\sigma_{10} - \sigma_{20})$$

$$b = (\sigma_{01} - \sigma_{21}) \quad , \quad g = -(\sigma_{01} + \sigma_{02} + \sigma_{20})$$

$P(z, i)$ — a function of the charge changing cross-section for a beam whose initial composition at the surface ($x = 0$) of the metal is denoted by z.

$N(z, i)$— a coefficient for negative exponential term analogous to $P(z, i)$

The values of $P(z, i)$ and $N(z, i)$ are given by Allision (10) (Table II-I).

TABLE II

Variation of $(\gamma_{He^0}/\gamma_{He^+})$ with energy in the range 40-400 kev

Energy (kev)	$(\gamma_{He^0}/\gamma_{He^+})_{cal}$ for Al	$(\gamma_{He^0}/\gamma_{He^+})_{obs}$* for brass	Percentage deviation
40	1·0	1·05	4·75
60	·99	1·05	5·7
80	·98	1·05	6·65
100	·92	1·05	12·8
200	1·02	1·05	2·86
300	1·02	...	...
400	1·0	...	...

*Values read from the experimental curve

It is evident that if the results obtained from Eqn. (10) hold, we should have,

$$\tfrac{1}{2}\Sigma\,\sigma_{if} > q.$$

If the original beam consists of helium atoms, the number of electrons produced by the loss process is $f_1 + f_2$. On the other hand, for an initial beam of He^+ ions, the number of such electrons is only f_2.

Proceeding is the usual manner, we obtain for an initial beam of He^+ ions of energy T bombarding a metal target,

$$\gamma_{He^+} = \frac{0{\cdot}25N}{\alpha} Q_{He^0}\left[f_0\infty \quad \frac{P(1,0)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}-\frac{N}{\alpha}q} + \frac{N(1,0)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}+\frac{N}{\alpha}q}\right]$$

$$+\frac{0{\cdot}25N}{\alpha} Q_{He^+}\left[f_1\infty + \frac{P(1,1)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}-\frac{N}{\alpha}q} + \frac{N(1,1)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}+\frac{N}{\alpha}q}\right]$$

$$+\frac{0\cdot25}{\alpha}(NQ_{He^{++}}+A)\left[f_{2\infty}+\frac{P(1,2)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}-\frac{N}{\alpha}q}\right.$$

$$\left.+\frac{N(1,2)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}-\frac{N}{\alpha}q}\right] \quad \ldots (11)$$

A similar calculation for He° beam gives

$$\gamma_{He^{\circ}}=\frac{0\cdot25N}{\alpha}Q_{He^{\circ}}\left[f_{0\infty}+\frac{P(0,0)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}-\frac{N}{\alpha}q}+\frac{N(0,0)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}+\frac{N}{\alpha}q}\right]$$

$$+\frac{0\cdot25}{\alpha}(NQ_{He^{+}}+A)\left[f_{1\infty}+\frac{P(0,1)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}-\frac{N}{\alpha}q}\right.$$

$$\left.+\frac{N(0,1)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}+\frac{N}{\alpha}q}\right]$$

$$+\frac{0\cdot25}{\alpha}NQ_{He^{++}}+A)\left[f_{2\infty}+\frac{P(0,2)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}-\frac{N}{\alpha}q}\right.$$

$$\left.+\frac{N(0,2)}{1+\frac{N}{2\alpha}\Sigma\sigma_{if}+\frac{N}{\alpha}q}\right].$$

To calculate secondary electron emission coefficients by He° and He^{+} bombardments, various charge changing collisional cross-sections and equilibrium fractions should be known. Since the equilibrium fractions of helium components for a beam of He° and He^{+} are known experimentally for an aluminium target, $\gamma_{He^{+}}$ and $\gamma_{He^{\circ}}$ are calculated for this target. Using Bohr's relation (16), σ_{01} (Al) is calculated from the experimental values of σ_{01} for helium beam passing through hydrogen gas (10). Similarly σ_{12} (Al) is calculated. σ_{10} and σ_{21} are obtained from the following relations:

$$\frac{\sigma_{10}}{\sigma_{01}}=\frac{f_{0\infty}}{f_{1\infty}} \text{ and } \frac{\sigma_{21}}{\sigma_{12}}=\frac{f_{1\infty}}{f_{2\infty}}.$$

The values of $f_{i\infty}$ are the obtained from experimental data of Hall (17) and Phillips (18). σ_{20} and σ_{02} are expected to be small for T < 400 kev and are neglected.

For energy less than 80 kev, the beam behaves as a three-component system consisting of He^0, He^+ and electrons. Hence for T < 80 kev, the expressions for γ_e for H^0 and H^+ are applicable also for a helium beam. In the absence of data for a metal target, experimental values of σ_{if} and $f_{i\infty}$ for helium beam passing through hydrogen and argon (10) respectively are used to calculate secondary electron emission coefficient. The calculated values of γ_e for an aluminium target bombarded by He^0 and He^+ in the energy range 25-400 kev are shown in Figs. (6) and (7). The experimental values obtained by Bourne *et al* (19) for Al

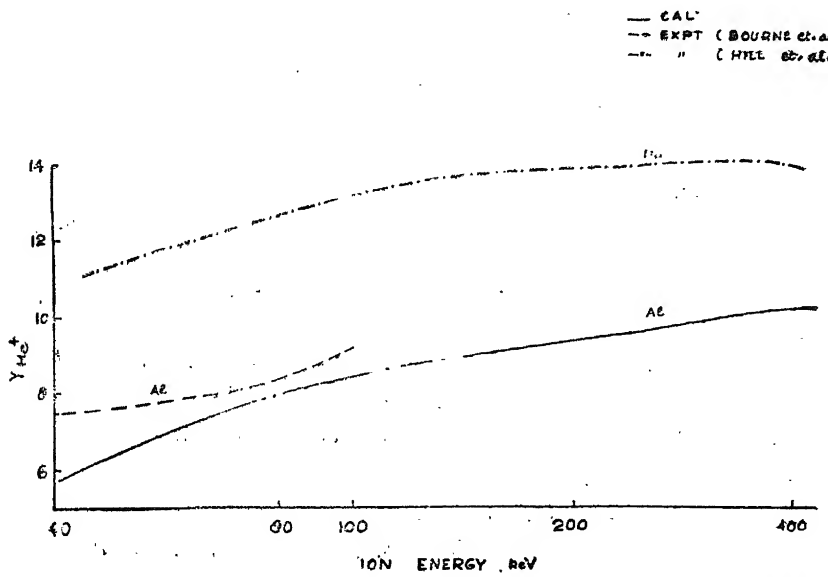

Fig. 6. Calculated variation of γ_{He^+} for aluminium with ion energy is compared with that obtained experimentally for Al and Mo targets.

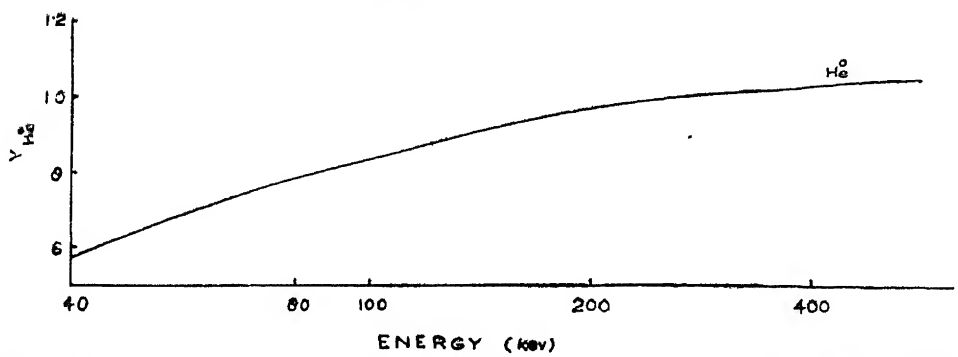

Fig. 7 Calculated variation of γ_{He^0} for aluminium with the energy of the bombarding helium atom.

and those of Hill *et al* (5) for Mo bombarded by He^+ in the energy range 20-120 kev and 43—426 kev respectively are also shown for comparison. In Table I, the ratio $\gamma_{He^0}/\gamma_{He^+}$ for an Al target is also given along with the experimental values obtnaied by Stier *et al* (14) for a brass target.

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SPUTTERING YIELDS OF SILVER AND ANGULAR DISTRIBUTION OF THE ATOMS SPUTTERED BY IONS OF NOBLE GASES

By

S. B. KARMOHAPATRO *and* A. V. NARASINHAM

Saha Institute of Nuclear Physics, Calcutta

INTRODUCTION

The studies of the phenomena of sputtering of the solid surfaces are of current interest, since it gives some ideas of the mechanism of the surface collision processes by energetic ions. Such studies of the metal surfaces are important for optimising the ion retention condition of a collector in an electromagnetic isotope separator and the use of the ions of noble gases gives informations about the improvement of the method of preparation of the gaseous isotopic targets, required in the experiments of nuclear physics.

Wehner[1] has reviewed the results of the experiments on the sputtering by low energy ions. Many authors[2-6,19] have given the results on the sputtering yield for energies below 100 kev and some of them present the angular distribution of the sputtered material. Almen and Bruce[7] have investigated various aspects of sputtering of metal by ions of noble gases as well as other ions in the light of the collection problems of the isotopes.

In the present paper, we have presented some preliminary results of the measurement of the sputtering yields of silver along with the angular distribution of the sputtered materials for ions of Helium, Neon, Krypton and Xenon at energies from 3-7 Kev.

EXPERIMENTAL METHOD

The system employed in the present experiment consists of a magnetic oscillation type arc discharge ion source with radial extraction arrangements with a 3/16″ diameter hole for extraction of the ions. The electronic circuits used in the experiment, are power supplies for the arc, filament and the accelerating voltage previously described by one of the authors.[8] The sputtering chamber with

the silver-110 *m* target and the ion source are shown in Fig. 1. 99-100% pure gases are introduced to the ion source. The number of ions, on the target, considered

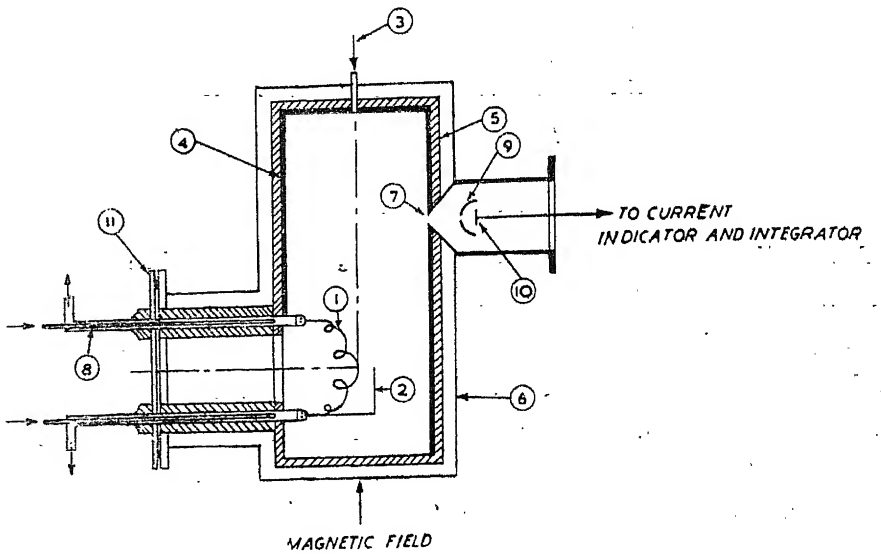

Fig. 1. Schematic diagram of the ion source and the sputtering chamber (1) 40 mil dia tungsten filament, (2) molybdenum plate, (3 gas inlet and electrical lead for anode, (4) graphite anode, (5) electrical insulation (Ergan), (6) metal casing, (7) ion exit slit, (8) water cooling tubes, (9) collector of the sputtered atoms, (10) Silver-110m target, (11) insulated flange for filament holders.

to be all as singly charged, was estimated by a current indicator and integrator. For each experiment with the different gases, the ion current was fixed at 10 μA by varying the arc condition, to avoid unequal heating of the target, which might cause variations in the total yield. The sputtering chamber was kept at a pressure 10^{-5} mm Hg in course of bombardment with the aid of a differential pumping arrangement.

The total activity in the collector cup was measured with a $1\frac{1}{2}''$ diameter NaI crystal scintillation spectrometor. The counts for each collector give the relative sputtering yield for ions of different energy and mass. The sputtering yield, S, (atom per ion) at 5 Kev for neon ions, found by Grϕnlund *et al*[4] as 5·5, was normalised to that estimated by the radioactivity in our experiment. This value of S at 5 Kev is reasonable when compared to that found by Laegried and Wehner[16] to be 1·98 at 600 ev. With respect to this absolute value, S was estimated for different ions of the noble gases of various energies in collision with silver surface.

The angular distribution was masured by the activity, with a Geiger counter, of the small pieces (1/8" dia) of the collector cup, cut uniformly in the radial direction.

In all cases, the target was bombarded by normally incident ions and after each bombardment the target was properly cleaned.

Since the sputtering chamber was within the magnetic field of the ion source itself, the number of the secondary electrons from the target was assumed to be negligible.

RESULTS

Fig. 2 shows the sputtering yield S as a function of the mass number of the noble gas ions in collision with silver. Figs. 3 and 4 show the energy versus yield

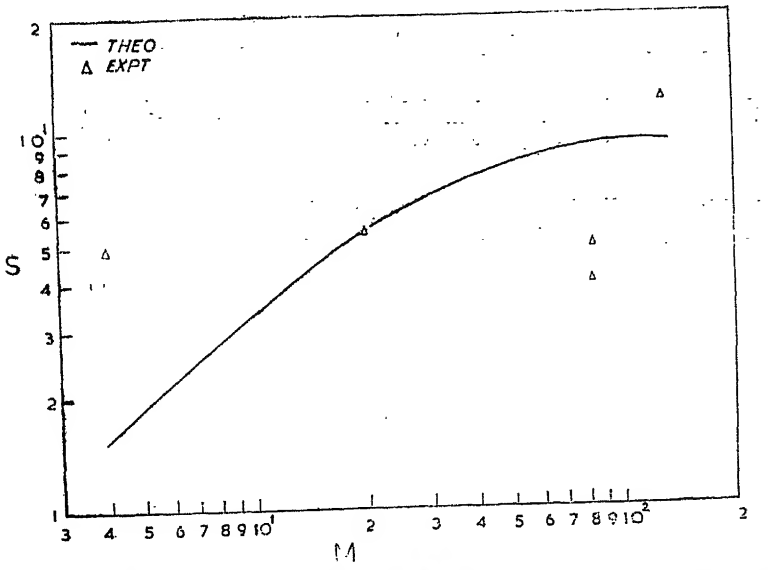

Fig. 2. Sputtering yield, S, as a function of mass of ion for normally incident 5 Kev ions on silver-110 m target.

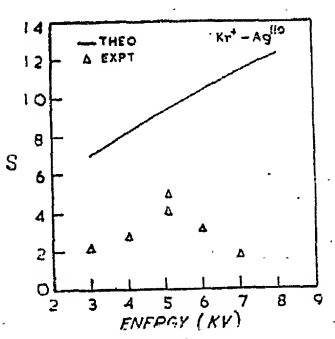

Fig. 3. Sputtering yield as a function of ion energy for Krypton ions normally incident on Silver-110 m target.

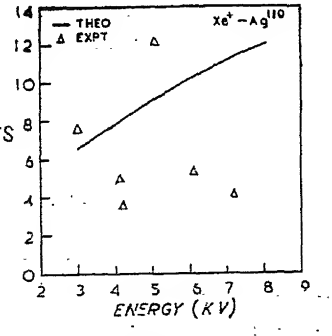

Fig. 4. Sputtering yield as a function of ion energy for Xenon ions normally incident on Silver-110 m target.

curve for krypton and xenon ions respectively. Fig. 5 is the polar diagram showing the angular distribution of the sputtered atoms for different ion masses

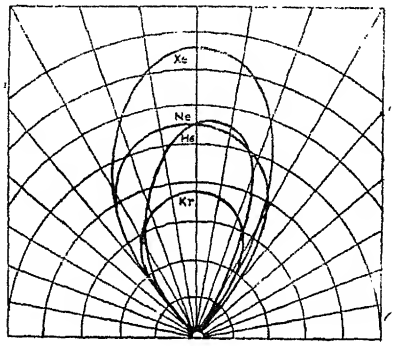

Fig. 5. Polar diagram of material sputtered from Silver-110 m by normally incident 5 Kev ions of Helium, Neon, Krypton and Xenon.

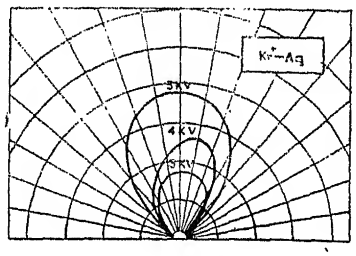

Fig. 6. Polar diagram of material sputtered from Silver-110 m by normally incident Krypton ions of different energies.

at 5 Kev. Figs. 6 and 7 are the polar diagrams showing the angular distribution of the materials sputtered by different energy ions.

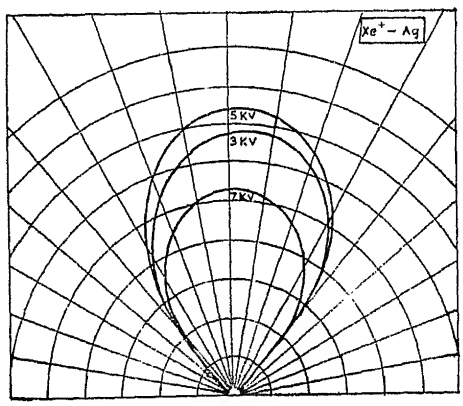

Fig. 7. Polar diagram of material sputtered from Silver-110 m by normally incident Xenon ions of different energies.

DISCUSSION

The theoretical models, explaining the sputtering process are mainly (1) the theory of evaporation and the (2) momentum transfer process.

The velocity of the sputtered atoms, determined by Wehner[17] mass dependence of the sputtering yields found by many authors and in the present work, the ejection patterns of the sputtered atoms in the preferential direction of a monocrystal observed by Wehner[1] and some other experimental results related to the sputtering phenomena cannot be explained by the evaporation theory.

The angular distribution of the sputtered materials measured by Seeliger and Sommermeyer[18], Brain *et al*[3], Grφnlund *et al*[4] seems to follow cosine law, so that the evaporation theory is supported.

The results of our measurements of the angular distribution of the sputtered material with the ion energy and mass are presented in Figs. 5, 6 7. The polar diagrams are drawn such that the enclosed areas in each diagram are proportional to the relative sputtering yield. All the diagrams show that the angular distribution seems to be over-cosine in this energy range. This is in agreement with that found by Rol *et al*[5] for 20 Kv ions in copper or by Holmstron and Knight[9] for argon ions in silver. For low energy ions the angular distribution is under-cosine, observed by Wehner *et al*[19]. From all these findings it seems that depending on the energy and masses of the ions and the targets along with the orientations of a polycrystalline target, the angular distribution is influenced, since in case of a monocrystal, the sputtering prefers a closed packed direction of the crystal plane. However, considering all the observations, the evaporation theory cannot explain the nature of change in the angular distribution of the sputtered materials.

It is difficult to comare the experimental results on the total sputtering yield S with the theoretical expectations, since the momentum exchange theory, based on different assumptions and subject to modifications for different cases, cannot be applied in one form, but it indicates the nature of its dependence on the different parameters like mass, energy etc. In the light of the hard sphere collision model worked out by mony authors[10-13], the mass dependence of the sputtering yield can be explained.

Following the treatment of Rol *et al*,[5] the sputtering yield is given by

$$S = K.\ 1/\lambda \quad \frac{M_1\, M_2\, E}{(M_1+M_2)^2}$$

where K is a constant, M_1, M_2 are masses of the incident ion and the target, E is the energy of the incident ions. The mean free path

$$\lambda = \frac{1}{\pi\, R^2 n_0}$$

where n_0 is the number of lattice atoms per unit volume and the collision radius

$$R = c\frac{a_0}{z_1^{2/3}+z_2^{2/3}} \quad ln\, \frac{z_1\, z_2}{\varepsilon_0}\frac{e^2\,(M_1+M_2)}{R\, E\, M_1}$$

as given by Seitz *et al*[15], where c is a constant, ε_0, the dielectric constant in vacuum, a_0, the first Bohr radius in hydrogen atom, e, the elementary charge, z_1 and z_2 are the atomic numbers of the incident ion and the target.

With a simple assumption that the sputtering happens in the first collision, the above expression is worked out. Assuming this model to be valid for the present energy range, we calculated the values of S for ions of different masses and energies. In calculating the theoretical values of S the value of K was chosen to give the best agreement with the experimental value of S (=5·5) for 5 Kv neon in silver, found by Grφnlund *et al*[4]. With this value of K, the values of the sputtering yields of silver, bombarded with ions of noble gases as a function of energy and masses of ions are shown in Figs. 2, 3, 4. The comparison shows that the agreement is better for Xe^+ than Kr^+ in silver. The general discrepancy may be due to (1) a multiple collision process instead of the single collision approximation used in the theory (2) the deviation of the value of K as shown by Almen and Bruce[7] from a constant one, approximated in the above theory. The major disagreement between the experimental results and the theoretical expectations lies in the fact that the value of S for krypton ions is relatively lower than that for neon ions; secondly the maximum near 5 Kev in the sputtering yield versus ion energy for krypton and xenon ions cannot be explained with this model. The maximum near 5 Kv with silver bombarded by Helium and Neon ions, observed by Grφnlund *et al*[4] is similar to our observations for Xenon and Krypton ions. For nitrogen and neon in collision with copper, Rol *et al*[5] has found a maximum for S near 15 Kev. The maximum may be explained by the two opposite effects of the increasing energy, one of which increases the probability and the other increases the mean free path, thus reducing the probability of collision. Then the nature and position of such maximum will depend upon the target material and the bombarding ion. From the few experimental results observed so far, such dependence cannot be uniquely established. The lower value of S for Krypton ions as compared with Neon ions in collision with silver surface also cannot be explained with the theory discussed above. Further examinations of more such data may be helpful for understanding the process in more detail.

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COLLISIONAL PROCESSES IN PLANETARY ATMOSPHERES

By

S. N. GHOSH *and* A. SHARMA

J. K. Institute of Applied Physics, University of Allahabad, Allahabad, India

ABSTRACT

Collisional processes between the constituent particles of the planetary atmosphere are considered with particular reference to that of the earth. Attempts have been made to explain certain upper atmospheric phenomena with the recently available data for collisional processes.

The collisions between constituent particles in a planetary atmosphere ions, etectrons and neutral particles-among themselves or with photons give rise to many atmospheric phenomena. For example in the earth's upper atmosphere, the ionized regions, aurora and airglow are all connected with the collisions between these particles. A scheme for understanding these phenomena related to planetary atmospheres may be developed as follows :

First, to postulate from geophysical and astrophysical observations the collisional processes which may possibly occur in the atmosphere of the earth or a planet.

Secondly, to select from the quantitative information of collisional processes, a single or a set of processes from the suggested ones for a particular atmospheric phenomenon.

It is, therefore clear that to understand in detail atmospheric phenomena in planets, precise knowledge of collisional processes is necessary. We have collected here important collisional processes which may occur in the planetary atmosphere with particular reference to that of the earth. These collisions can be classified into two catagories ;

(1) Photon Collisions, that is to say, collisions initiated by photons,

(2) Particle Collisions, in which particles collide to produce a reaction.

1. Photon Collisional Processes

These processes are classified as follows :

1. Photo-ionization and preionization

$$X + h\nu \rightarrow X^+ + e \; ; \; X + h\nu \rightarrow X'', \; X'' \rightarrow X^+ + e$$

2. Photo-detachment

$$X^- + h\nu \rightarrow X + e$$

3. Photodissociation and predissociation

$$XY + h\nu \rightarrow X + Y \; ; \; XY + h\nu \rightarrow XY', \; XY' \rightarrow X + Y$$

4. Resonance fluorescence and scattering

$$X + h\nu \rightarrow X^*, \; X^* \rightarrow X + h\nu$$

Important reactions of these processes in the earth's upper atmosphere are collected in Table I. Certain phenomena related to the above collisional processes are discussed below.

TABLE I

Information regarding photon collisional processes in earth's atmosphere

Process	Reaction		Threshold λ (A)	Coefficient or cross-section	Ref.	Remark
Photoionization	$O + h\nu \rightarrow O^+ + e$	(4)	910 (13·5 ev)	$\sigma_i = 5{\cdot}01 \times 10^{-18}$ cm^2	(2)	
	$N + h\nu \rightarrow N^+ + e$		847 (14·5 ev)	$\sigma_i = 3{\cdot}16 \times 10^{-18}$ cm^2	(2)	
	$O_2 + h\nu \rightarrow O_2^+ + e$	(4)	1019 (12·2 ev)	$\sigma_i = 1{\cdot}6 \times 10^{-18}$ cm^2	(7)	First ionization potential 12·2 ev
		(8)	1027 (12·07 ev)	$\sigma_i = 1{\cdot}54 \times 10^{-18}$ cm^2	(8)	First ionization potential 12·07 ev
		(8)	1025 (Layman-β)	$\sigma_a = 1{\cdot}54 \times 10^{-18}$ cm^2	(8)	
	$N_2 + h\nu \rightarrow N_2^+ + e$	(4)	795 (15·5 ev)	$\sigma_i = 4{\cdot}8 \times 10^{-17}$ cm^2	(7)	
	$NO + h\nu \rightarrow NO^+ + e$	(9)	1343 (9·23 ev)	$\sigma_i = 1 \times 10^{-18}$ cm^2	(9)	Between 1060-1300A, σ_i is of order 10^{-18} cm^2 Error is 50%
				$\sigma_a = 3{\cdot}7 \times 10^{-18}$ cm	(9)	
	$NO + h\nu \rightarrow NO^+ + e$		1216 (L_α)	$\sigma_i = 2 \times 10^{-18}$ cm^2	(5)	
	$Na + h\nu \rightarrow Na^+ + e$	(8,1)	2438 (5·1 ev)			
Preionization	$O_2 + h\nu \rightarrow O'_2 \rightarrow O_2^+ + e$	(4)	770 (16·1 ev)	$\sigma_i = 1{\cdot}1 \times 10^{-17}$ cm^2	(7)	
	$N_2 + h\nu \rightarrow N'_2 \rightarrow N_2^+ + e$	(4)	661 (18·7 ev)	$\sigma_i = 2{\cdot}8 \times 10^{-17}$ cm^2	(7)	
	$O_2 + h\nu \rightarrow O''_3 \rightarrow O_2^+ + e$	(4)	732 (16·9 ev)	$\sigma_i = 2{\cdot}08 \times 10^{-17}$ cm^2	(7)	
	$O_2 + h\nu \rightarrow O_2''' \rightarrow O_2^+ + e$	(4)	682 (18·2 ev)	$\sigma_i = 1{\cdot}98 \times 10^{-17}$ cm^2	(7)	
	$O + h\nu \rightarrow O' \rightarrow O^+ + e$	(4)	732 (16·9 ev)	$\sigma_i = 1{\cdot}04 \times$ cm^2		
	$O + h\nu \rightarrow O'' \rightarrow O^+ + e$	(4)	665 (18·5 ev)	$\sigma_i = 1{\cdot}43 \times 10^{-17}$ cm^2	(7)	
Photodissociation	$O_2 + h\nu \rightarrow O(^3P) + O(^1D)$	(1)	1760	$\sigma_a = 2 \times 10^{-17}$ cm^2	(1)	Schuman-Runge continuum commences at 1760

	$O_2+h\nu\rightarrow O(^3P)+O(^3P)$	(1)	2420	$\sigma_a = 10^{-23}-10^{-24}cm^2$ (1)	Herzberg continuum commences at 2420
	$O_3+h\nu\rightarrow O_2+O(^1D)$	(1)	2550	$\sigma_a = 2{\cdot}98\times10^{-18}$ cm^2 (9)	Strong Hartley continuum commences at 2550
	$O_3+h\nu\rightarrow O_2+O(^3P)$	(1)	6100		Weak Chappins continuum commences at 6100
	$N_2^+ + h\nu\rightarrow N+N^+$				Yield of atomic nitrogen is very small
	$NO_2+h\nu\rightarrow NO+O$				
	$H_2O+h\nu\rightarrow OH(X\,^2\pi)+H$	(1)	2400	$\sigma_a = 3{\cdot}72\times10^{-18}$ cm^2(1650A)(9) $\sigma_a = 7{\cdot}44\times10^{-18}$ cm^2(1250A)	
	$CO_2+h\nu\rightarrow CO+O(^3P)$	(1)	1690	$\sigma_a = 5{\cdot}58\times10^{-19}$ cm^2 $\sigma_a = 7{\cdot}44\times10^{-19}$ cm^2 $\sigma_a = 3{\cdot}72\times10^{-17}$ cm^2	
	$N_2O+h\nu\rightarrow N_2+O(^3P,^1D)$	(1)	3070		
	$N_2O+h\nu\rightarrow NO+N(^4S)$	(1)	2400	$\sigma_a = 7{\cdot}44\times10^{-20}$ cm^2 $\sigma_a = 7{\cdot}44\times10^{-18}$ cm^2 $\sigma_a = 7{\cdot}44\times10^{-17}$ cm^2	
Photodetachment	$O^- + h\nu \rightarrow O + e$			$\beta = 1\times10^{-15}$cm^3/sec (4)	
	$O_2^- + h\nu\rightarrow O_2 + e$			$\beta = 1\times10^{-16}$cm^3/sec (4)	
Predissociation	$N_2(X'\,\Sigma_g^+)+h\nu\rightarrow N_2(a\,^1\pi g)$ $\lambda\lambda$1200-1250 $N_2(a\,^1\pi_g)\rightarrow N+N$			$\sigma_a = 1\times10^{-20}$cm^2	
	$NO+h\nu\rightarrow$ NO ($A^2\Sigma^+$, $C^2\Sigma^+$) NO ($A^2\Sigma^+$, $c^2\Sigma^+$)$\rightarrow N+O$			$\sigma_a = 3{\cdot}72\times10^{-19}$ cm^2 (9)	
Resonance fluorescence	$N_2^+ + h\nu\rightarrow N_2^{+*}\rightarrow N_2^+ + h\nu$ $Na+h\nu\rightarrow Na^*\rightarrow Na+h\nu$				

(1) Bates (1953), (2) Dalgarno *et al* (1960), (3) Herzberg (1950), (4) Mitra (1952),
(5) Nicolet *et al* (1960), (6) Watanabe (1954), (7) Watanabe (1958), (8) Watanabe *et al* (1955), (9) Watanabe *et al* (1953)

Hulburt (1938), Bates and Hoyle (1948), Vegard (1923, 1938) and recently Friedman (1959) suggested that soft X-rays emanated from the sun may produce the E-layer. The total amount of solar X-ray energy obsorbed in the E-layer is calculated from the energy at the top of the earth's atmosphere obtained from the rocket-borne experiments and their transmission through atmosphere. Assuming that the whole of energy absorbed in the E-layer is utilized in the ionization of atmospheric gases, the rate of ionization produced by (1) absorbed X-rays, (2) ejected photo-electrons produced by X-rays, and (3) Auger effect inducted by X-rays is calculated by Ghosh and Shardanand (1960) (Table II)

TABLE II

Gas	K-shell Ionization (cm^{-2}-sec^{-1} col^{-1})	L-shell ionization (cm^{-2} sec^{-1} col^{-1})	Valence shell Ionization (cm^{-2} sec^{-1} col^{-1})	Ionization by Auger Effect	
				Direct electron ejection (cm^{-2} sec^{-1} col^{-1})	From X-ray emission (cm^{-2} sec^{-1} col^{-1})
Oxygen	$2{\cdot}5 \times 10^{6}$	$1{\cdot}6 \times 10^{8}$	$2{\cdot}2 \times 10^{9}$	$1{\cdot}2 \times 10^{6}$	$2{\cdot}4 \times 10^{7}$
Nitrogen	$1{\cdot}8 \times 10^{7}$	$2{\cdot}2 \times 10^{8}$	$3{\cdot}4 \times 10^{9}$	$8{\cdot}8 \times 10^{6}$	$2{\cdot}2 \times 10^{8}$
Total	$2{\cdot}0 \times 10^{7}$	$3{\cdot}8 \times 10^{8}$	$5{\cdot}6 \times 10^{9}$	$1{\cdot}0 \times 10^{7}$	$2{\cdot}4 \times 10^{8}$

It is concluded that valence shell ionization is the main process for X-ray ionization in the E-layer.

From the X-ray photoionization one can also calculate the distribution of N_2 molecules in the earth's upper atmosphere which is not so definitely known as that of O_2. N_2 distribution has been calculated by Ghosh and Sharma (1961*a*). In this calculation, information regarding the observed variation of X-ray intensity with altitude obtained from rocket-borne experiments, the altitude of 95% absorption and, the distribution of O atoms and O_2 molecules were utilized.

If it is assumed that solar X-ray radiation is absorbed by O, O_2 and N_2 in the earth's atmosphere, the number of X-ray quanta absorbed upto the depth of penetration is given by

$$n(h\nu) = n(h\nu)\,[k\nu\,(O)\,N(O) + k\nu\,(O_2)\,N(O_2) + k\nu\,(N_2)\,N(N_2)]$$

where,

$n(h\nu)$—number of X-ray photons between wave length region 6 – 10A

$k\nu$ (O), $k\nu$ (O_2), $k\nu$ (N_2)—average absorption cross-sections for O, O_2 and N_2 respectively between 6–10A

N(O), N(O_2), N(N_2) – number of O, O_2 and N_2 molecules respectively per cm^2 column above the depth of penetration.

Hence, the number of N_2 molecules per cm^2 column above the depth of penetration is given by

$$N(N_2) = \frac{1 - k\nu\,(O)\,n(O) - k\nu\,(O_2)\,N(O_2)}{k\nu\,(N_2)}$$

substituting the relevant data the number of N_2 molecules above the depth of penetration are obtained and are given in table (III)

TABLE III

Altitude (km)	Number of N_2 molecules above h(/cm^2 column) (1)	Number of N_2 molecules above h(/cm^2 column) (2)	Calculated number of N_2 molecules above h(/cm^2 column)
95	$4{\cdot}0 \times 10^{19}$	$3{\cdot}8 \times 10^{19}$	$1{\cdot}1 \times 10^{19}$
100	$1{\cdot}4 \times 10^{19}$	$1{\cdot}2 \times 10^{19}$	$7{\cdot}7 \times 10^{18}$
105	$8{\cdot}3 \times 10^{18}$	$7{\cdot}0 \times 10^{18}$	$4{\cdot}3 \times 10^{18}$
110	$3{\cdot}2 \times 10^{18}$	$2{\cdot}6 \times 10^{18}$	$3{\cdot}4 \times 10^{18}$
120	$9{\cdot}0 \times 10^{17}$	$7{\cdot}0 \times 10^{18}$	$1{\cdot}9 \times 10^{18}$

(1) Kallman *et al* (1956) (2) Miller (1957)

Photo-dissociation processes in the Martian atmosphere where the main constituents are N_2 and CO_2 molecules have been considered by Ghosh and Sharma (1963). Comparing the relative importance of the following processes for N atom formation.

$$N_2 + h\nu \ (1076A < \lambda < 1267A) \rightarrow N + N \text{ (Predissociation)}$$

and $$N_2^+ + e \rightarrow N' + N' \text{ (Dissociative recombination)}$$

It has been concluded that below 270 km predissociation predominates over dissociative recombination of N_2^+ ions with electrons.

The dissociation of CO_2 is accomplished by direct photo-dissociation. Watanabe *et al* (1953) have interpreted the continua in the absorption spectrum of CO_2 as follows :

Region (A)	Wavelength for peak absorption (A)	Photodissociated products
1750 – 1400	1475	$CO(^1\Sigma) + O(^3P)$
1480 – 1250	1332	$CO(^1\Sigma) + O(^1D)$
1175 – 1050	1119	$CO(^1\Sigma) + O(^1S)$

The rate of photo-dissociation of the ith constituent in a planetary atmosphere at an altitude z is given by (Ghosh and Sharma, 1963),

$$J_{iz} \cdot n_{iz} = \gamma \left[\sum_{\nu} n(h\nu)_{\infty} \cdot K_{\nu z} \cdot k_{\nu i} \right] n_{iz}$$

and $$J_{iz} = \gamma \sum_{\nu} n(h\nu)_{\infty} \cdot K_{\nu z} \cdot k_{\nu i}$$

where,

J_{iz} – probability of dissociation of the ith constituent at the altitude z.

$n(h\nu)_{\infty}$ – photon flux of wave number ν at the top of the atmosphere from the sun.

$k_{\nu i}$ – absorption cross-section of the ith constituent for the wave-number ν.

$K_{\nu z}$ – transmission coefficient of the atmosphere at the altitude z for the wavenumber ν.

n_{iz} – concentration of the ith contituent at the altitude z.

γ – ratio of dissociated molecules to the adsorbed quanta.

The summation is to be carried over the wavelength region which produces the dissociation of the ith constituent. The transmission coefficient $K_{\nu z}$ in the above expression is defined by

$$K_{\nu z} = \exp - \left[\sum_i N_{iz} \cdot k_{\nu i}\right]$$

where, N_{iz} is the number of molecules of the ith constituent per cm^2 column above z km altitude. The summation is to be carried over for all the constituents of the atmosphere which absorb the radiation of wavenumber ν. Approximate altitude distribution of the equilibrium concentrations of N, N_2, CO, O and CO_2 has been calculated by Ghosh and Sharma. In their calculation, they have considered the photo-dissociation of N_2 and CO_2 and recombination by the following reactions :

$$N + N + M \rightarrow N_2 + M$$

$$CO + O + M \rightarrow CO_2 + M$$

It has been found that in the Martian atmosphere CO_2 and N_2 are completely dissociated above 120 km and 250 km respectively.

2. Particle Collisional Processes

Particle collissional processes can be devided into two classes :

1. Elastic collisions, in which the internal motions of the colliding particles do not change,
2. Inelastic collisions, in which the internal motions of the colliding particles are altered.

Elastic Collisions

The information regarding the elastic collisions between atmospheric particles is of importance in many phenomena *e. g.* diffusion, conductivity, and radio wave absorption in the ionosphere. Since in an elastic collision transfer of momentum takes place, processes connected with such collisions are characterised by momentum transfer cross-section Q or by an average momentum transfer cross-section $\bar{Q}$, if the distribution of velocities of the colliding particles is considered.

In connection with the studies of temporal variations of electron density in the ionosphere, aurora, meteoric trails and artificial electron clouds created in upper atmosphere, the diffusion coefficient D of electrons should be known, which is given by

$$D=(1/3n)\ (V/Q)$$

where, V is the electron velocity and n the gas number density. However, the collisional frequency ν $(=VQ\ n\ sec^{-1})$ of electrons with atmospheric particles is an important parameter in the theory of radio wave propagation. The data regarding the collisional frequency of electrons with ions and also with molecules are collected in Table IV.

TABLE IV

Gas	Energy range of electrons (ev)	Expression for collisional frequency ν sec^{-1}	References
N_2	·05 – ·005	$(2{\cdot}5 \times 10^{-9}\ u^{1/2} + 1{\cdot}2 \times 10^{-7}\ u)n$	(1)
O_2	0·2 – 0·03	$(4 \times 10^{-9}\ u^{1/2} + 5 \times 10^{-8}\ u)n$	(2)
Air	1 – ·005	$1{\cdot}22 \times 10^{-7}\ u\ n$	(2)
H_2O	Thermal Energy	$10^{-7}\ u^{-1/2}\ n$	(3)
O	,,	$2{\cdot}03 \times 10^{-7}\ u.n$	(2)
Positive Ions	,,	$\bar{\nu}=\{34 + 4{\cdot}18 \log (T^3/n_e)\}\ T^{-3/2}n_i$	

u—electron energy (eV) ; n – gas particle density

T—gas temperature (°K) n_e—electron density

n_i – ion density

(1) Phelps et al (1959) (2) Dalgarno (1961) (3) Altshuler (1957)

The momentum transfer cross-section for collisions between positive ions and neutral gas molecules can be obtained from the mobility of ions in gases. The later are collected in Table V. Their variation with temperature is given in the next table.

TABLE V*

Mobility of ion in gases

Ion / Gas	He	Ne	A	Kr	Xe	N_2	H_2	CO
Li	38·6	30·0	11·4	9·4	7·3	9·3	15·6	5·5
Na	41·9	26·8	11·5	9·3	7·5	10·1	17·3	8·1
K	41·0	27·4	11·7	9·6	7·4	10·2	17·4	8·8
Rb	39·3	27·2	11·7	9·5	7·4	10·3	17·5	8·8
Cs	36·3	25·5	11·5	9·5	7 4	10·3	17·6	8·9
A	39·9	—	—	—	7·7	—	—	—
Hg	37·0	—	—	—	—	10·1	—	—

* Dalgarno *et al* (1958 *a*)

TABLE VI*

Variation of Mobility of Positive ions in their Parent gases with temperature

Gas Temp. (°K)	H	O′	He	O_2	CO	H_2
0	26·3	2·0	21·5	—	—	—
100	16·7	1·9	13·4	—	—	—
200	13·6	1·7	12·0	—	—	—
300	12·4	1·6	10·8	2·2	1·6	13·4
500	10·2	1·3	8·7	—	—	—

O′ – data on O are uncertain

* – Dalgarno (1958 *b*)

In the upper atmosphere charge exchange reactions occur at low ion energy of the order of a few tenths of a volt. However the experimental determination of their cross-sections is confined to high ion energy of the order of several KeV and on the low enery side upto a few tens of eV. Information regarding charge exchange cross-sections at low ion energies can be obtained from the mobility of ions in gases and have been obtained by Ghosh and Sharma (1962 *b*).

The mobility of ions in a gas depends on long-range (polarization and dispersion) and short-range (exchange) forces. The magnitude of the former type of forces, which are predominant at very low temperatures ($T << 273°K$), can be theoretically calculated (Mason *et al*, 1959). The latter type of forces, which are predominent at high temperatures, can be estimated from the scattering of ions by gas molecules. Since, for symmetric charge exchange reactions (unlike unsymmetric ones) the cross-sections at low ion energy are large, the effect of charge exchange in low energy ions is more pronounced when ions move in their parent gases.

From above, it is clear that the temperature dependence of ionic mobility is important with reference to the influence of ion-molecule forces on the motion of ions. Biondi and Chanin (1954, 1957) measured the mobility of ions in their parent gases at three temperatures (77°, 195° and 300°K).

Dalgarno *et al* (1958 *a*) has shown that the reduced mobility k, of an ion is given by,

$$k = \frac{2{\cdot}10 \times 10^4}{P\sqrt{(\mu T)}} \text{ cm}^2 \text{ (volt)}^{-1} \text{ sec}^{-1} \qquad (1)$$

where

μ – reduced mass of ion and gas molecule in units of proton mass

T – absolute temperature

P – momentum transfer cross-section in units of a_0^2

Using the above equation and from experimental data of variation of ionic mobility with temp. obtained by Biondi and Chanin (1954, 1957), the value of P is calculated. Where the experimental data are not available, the theoretical data of Dalgarno *et al* (1958 *a*) and Lynn and Moiseiwitsch (1957) on ionic mobility are utilized. P is plotted against the absolute temperature for He^+ in He, Ne^+ in Ne and A^+ in A (Fig. 1). The curve shows that P decreases vary rapidly with increase of

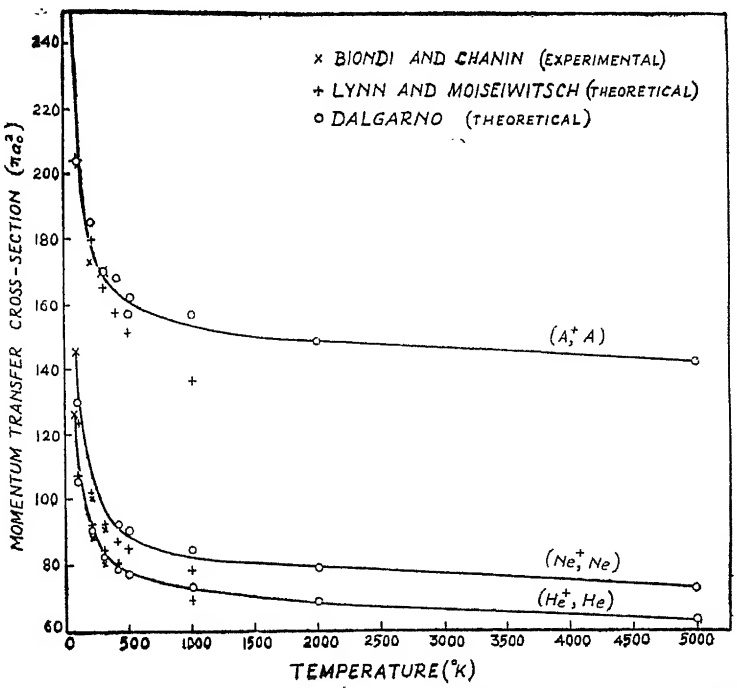

Fig. 1. Variation of momentum transfer cross-section P with temperature for He^+ – He, Ne^+ – Ne and A^+ – A

temperature from T=O°K. After certain temperature, the decrease is very slow and then becomes steady. The temperature, at which rapid decrease in the value of P changes in to slow and steady decrease, is called the *Transition Temperature*. At the transition temperature the short-range and long-range forces become equal. Above this temperature, the short-range forces predominate and therefore the study of the mobility of ions in a gas at higher temperature reveals information regarding charge exchange cross-section of ions and neutral gas molecules. The value of the transition temperature for above three cases is about 400°K.

Using mobility data of Biondi and Chanin (1954, 1957), P is calculated from Eqn. (1) at three temperatures and are plotted against X/p_0 in Figs. 2—4. It is found that the following empirical relation

$$P(X/p_0, T) = P(O, T)\,[1 + (\alpha + \beta\, T^3)\, X/p_0]^{1/2} \qquad (2)$$

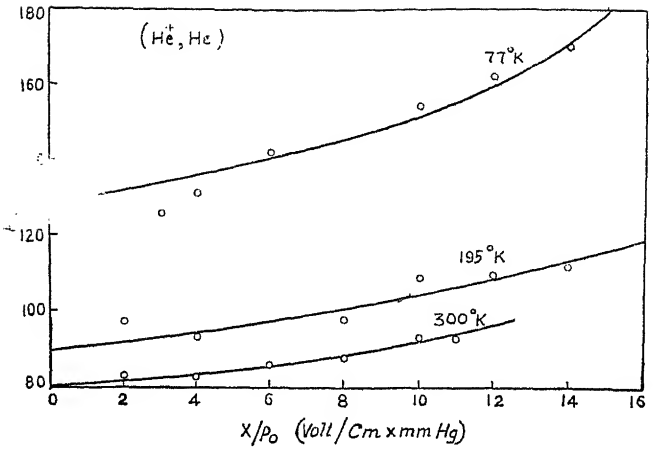

Fig. 2. Variation of momentum transfer cross-section P with X/p_0 for He+ – He.

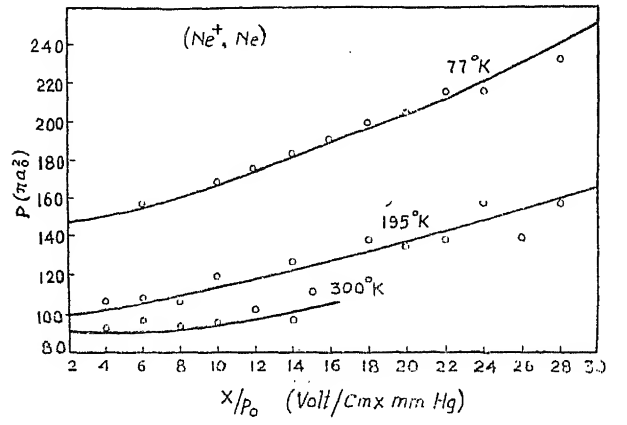

Fig. 3. Variation of momentum transfer cross-section P with X/p_0 for Ne+ – Ne.

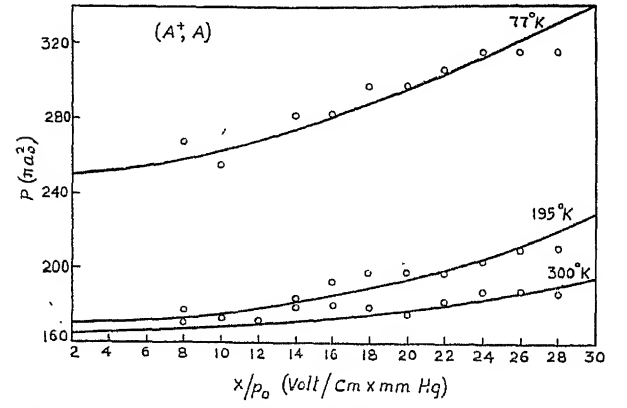

Fig. 4. Variation of momentum transfer cross-section P with X/p_0 for A+ – A.

fits the experimental data satisfactorily for high value of X/p_0 where P_0 is the value of P at $X/p_0 = 0$ and is determined from Bradbury and Chanin's. The values of α and β are determined for He^+ in He, Ne^+ in Ne and A^+ in A and are given in Table VII. Since the constants α and β are very small, Eqn. (2) possesses the experimental behaviour of P being independent of X/p_0 when its value is low.

Dalgarno 1957) has shown theoretically that for He^+, He ; Ne^+, Ne and A^+, A P_0 varies with temperature according to the following relation

$$P_0(T) = A - B \log_{10}T + C (\log_{10}T)^2 \qquad (3)$$

Mason *et al* (1959) have also obtained theoretically similiar variation of $P_0(T)$ for diatomic molecular ion H_2^+ in H_2. The values of the constants A, B and C for inert gas ion cases are also given in Table VII.

TABLE VII

Ion and Gas	A	B	C	α	β
He^+, He	737·10	508·73	98·51	$5{\cdot}3 \times 10^{-2}$	$1{\cdot}00 \times 10^{-9}$
Ne^+, Ne	5 8·95	287·47	44 76	$4{\cdot}55 \times 10^{-2}$	$0{\cdot}86 \times 10^{-9}$
A^+, A	1897·00	1442·94	301·18	$2{\cdot}5 \times 10^{-2}$	$1{\cdot}00 \times 10^{-9}$

It may be noted that for motion of an ion in parent gases, the transfer of momentum takes place due to the charge exchange (symmetric) between ions and gas molecules. Therefore, from Eqns. (1) and (2), one can obtain information regarding the momentum transfer cross-section and hence the charge exchange cross-section at low ion energy.

3. Inelastic Collisional Processes

Inelastic collisional processes are as follows

1. Excitation by collision or collisional de-activation,

   $X' + Y \rightarrow X + Y^*$ (Collisional excitation)

   $X + Y^* \rightarrow X' + Y$ (Collisional de-activation)

2. Ionization or detachment by collision,

   $X' + Y \rightarrow X + Y^+ + e$ (Ionization)

   $X' + Y^- \rightarrow X + Y + e$ (Detachment)

3. Exchange of internal energy,

$$X^* + Y \rightarrow X + Y^*$$

$$Y^* \rightarrow Y + h\nu \qquad \text{(Sensitized flourescence)}$$

$$X + Y^* \rightarrow X^* + Y \qquad \text{(Quenching)}$$

4. Capture of free electron,

$$X^+ + e \rightarrow X^* + h\nu \qquad \text{(Radiative recombination)}$$

$$X^+ + e \rightarrow X^{**},$$

$$X^{**} \rightarrow X^* + h\nu \qquad \text{(Dielectronic recombination)}$$

$$XY^+ + e \rightarrow X^* + Y^* \qquad \text{(Dissociative recombination)}$$

$$X + e \rightarrow X^- + h\nu \qquad \text{(Radiative attachment)}$$

$$X + e \rightarrow X^{-**}, X^{-**} \rightarrow X^{-*} + h\nu \qquad \text{(Dielectronic attachment)}$$

$$XY + e \rightarrow X + Y^- \qquad \text{(Dissociative attachment)}$$

$$X^+ + e + M \rightarrow X + M \qquad \text{(Three-body recombination)}$$

$$X + e + M \rightarrow X^- + M \qquad \text{(Three-body attachment)}$$

5. Exchange of electrons,

$$X^+ + X \rightarrow X + X^+ \qquad \text{(Symmetric charge transfer)}$$

$$X^+ + Y \rightarrow X + Y^+ \qquad \text{(Asymmetric charge transfer)}$$

$$X^+ + Y^- \rightarrow X^* + Y^* \qquad \text{(Mutual neutralization)}$$

$$X^+ + Y^- + M \rightarrow X + Y + M \qquad \text{(Three-body ionic neutralization)}$$

$$X^+ + Y \rightarrow X + Y^+ \qquad \text{(Non-reasonance charge transfer)}$$

6. Exchange of ions and atoms,

$$XY^+ + Z \rightarrow X + YZ^+ \qquad \text{(Ion-atom interchange)}$$

$$XY + Z \rightarrow X + YZ \qquad \text{(Chemical reaction)}$$

In the above reactions (*) or dash (') signifies an excited (translationally, electronically vibrationally or rotationally) molecule.

Important inelastic reactions in the earth's upper atmosphere and their coefficients are collected in Tables VIII, IX and X.

Certain phenomena in planetary atmosphere connected with inelastic collisional processes are given below. These phenomena will be considered afterwards.

(*i*) Excitation of λ5557 line in the night airglow.

(*ii*) Excitation of λ6300 line in the night airglow.

(*iii*) Excitation of Na – D lines in the night airglow.

(*iv*) Identification of reaction products resulting from dissociative recombination of N_2^+ ions with electrons.

(*v*) Excitation of Spectra by ion bombardment.

(*vi*) Ion-atom interchange reactions. The distribution of positive ions in the F-region of the ionosphere.

(*vii*) Photochemical reactions in the Martian atmosphere.

(*viii*) An experimental method of studing reaction between free atoms and molecules.

4. Certain Atmospheric Phenomena Connected with Inelastic Collisional Processes.

(*i*) Excitation of λ5577 line.

The excitation of λ5557 line in the night airglow may be produced by a reaction of the following type (Ghosh and Sharma, 1961*b*).

(*a*) Bimolecular reaction involving neutral particles.

(*b*) Bimolecular reaction involving ions and electrons.

(*c*) Trimolecular reactions.

A bimolecular reaction involving neutral particles can be represented as follows.

$$X + YO \rightarrow XY + O'$$

where, X and Y are atoms or molecules. From consideration of energy,

TABLE VIII

Capture of free electron

Process	Reaction	Temperature °K or electron energy eV	Rate co-officient $cm^3.sec^{-1}$	Reference	Remark
Radiative recombination	$O^+ + e \rightarrow O' + h\nu$	250 °K	$3{\cdot}4 \times 10^{-12}$	(1)	The temperature variation given in (1)
$X^+ + e \rightarrow X + h\nu$		2000 °K	$0{\cdot}8 \times 10^{-12}$	(1)	
	$H^+ + e \rightarrow H' + h\nu$	250 °K	$4{\cdot}8 \times 10^{-12}$	(2) and	
		2000 °K	$1{\cdot}3 \times 10^{-12}$	(3)	
	$N^+ + e \rightarrow N' + h\nu$ $O_2^+ + e \rightarrow O_2' + h\nu$ $N_2^+ + e \rightarrow N_2' + h\nu$ $NO^+ + e \rightarrow NO' + h\nu$		$\sim 10^{-12}$	(16)	Estimated
Dielectronic recombination.					
$X^+ + e \rightarrow X^{**} + c$			$\sim 10^{-12}$	(4) and (5)	Estimated
$X^{**} \rightarrow X^* + h\nu$	$A^+ + e \rightarrow A^{**} + h\nu$	300 °K	5×10^{-11}	(6)	Experimentally observed.
Dissociative recombination	$N_2^+ + e \rightarrow N + N$	300 °K	$1{\cdot}4 \times 10^{-6}$	(7)	Experimental
$XY^+ + e \rightarrow X + Y$		2500 °K	$1{\cdot}4 \times 10^{-7}$	(8)	,,
		300 °K	$1{\cdot}4 \times 10^{-6}$	(9)	,,
		92 °K	$6\,7 \times 10^{-6}$	(10)	,,
		300 °K	$8{\cdot}5 \times 10^{-7}$	(10)	,,
		400 °K	4×10^{-7}	(11)	,,
		480 °K	4×10^{-7}	(22)	,,

	$O_2^+ + e \rightarrow O + O$	2500 °K	$2{\cdot}5 \times 10^{-7}$	(12)	
		480 °K	1×10^{-8}	(22)	
	$NO^+ + e \rightarrow N + O$	5000 °K	$\sim 10^{-9}$	(13)	Observed from the reverse process.
		480 °K	1×10^{-8}	(22)	
Radiative attachment $X + e \rightarrow X^- + h\nu$	$O + e \rightarrow O^- + h\nu$	100 °K	$1{\cdot}4 \times 10^{-15}$	(14)	Experimental
		2000 °K	$1{\cdot}2 \times 10^{-15}$	(14)	
	$O_2 + e \rightarrow O_2^- + h\nu$				
	$H + e \rightarrow H' + h\nu$			(15)	Theoretical
Dielectronic attachment $X + e \rightarrow X^{-**}$ $X^{**} \rightarrow X^{-*} + h\nu$			$\sim 10^{-15}$	(16)	Estimated
Dissociative attachment.	$O_2 + e \rightarrow O + O^-$	4·5 eV	$\alpha_{max} = 4 \times 10^{-11}$	(20)	Experimental. Threshold of electron enery is 3·5 eV, (17), (18) and (19)
Three-body recombination $X^+ + e + M \rightarrow X + M$			$2 \times 10^{-10} \times p$	(5)	p is the pressure of the gas in mm of Hg.
Three-body attachment. $X + e + M \rightarrow X^- + M$	$O_2 + e + O_2 \rightarrow O_2^- + O_2$	0·09 eV at 300 °K	$5 \times 10^{-30} cm^6 . sec^{-1}$	(21) and (19)	The maximum value of the rate coefficient is given.
		Thermal electrons $2{\cdot}8 \times 10^{-30}$ $cm^6.sec^{-1}$.			

(1) Bates *et al*, 1939. (2) Burges, 1958. (3) Seaton. 1959. (4) Massey *et al*, 1943. (5) Massey 1952. (6) Garton *et al*, 1960. (7) Biondi and Brown, 1949. (8) Sayers, 1953. (9) Faire *et al* 1958. (10) Bialeke *et al*, 1958. (11) Faire *et al*, 1959. (12) Sayers, 1961. (13) Lin, 1959. (14) Branscomb *et al*, 1958. (15) Massey, 1949. (16) Dalgarno, 1961. (17) Craggs *et al*, 1957. (18) Tozer *et al*, 1958. (19) Chanin *et al*, 1959. (20) Thompson, 1959. (21) Hurst *et al*, (1959). (22) Ghosh *et al*, 1962*a*.

TABLE IX

Exchange of Electrons

A. Low Energy

Process	Reaction	Ion energy eV	Rate coeffi. (Cross-section cm^2)	Reference	Remarks
Symmetric Resonance charge Transfer	$H^+ + H \rightarrow H + H^+$	0·1	$5{\cdot}98 \times 10^{-15}$	(1)	
		1·0	$4{\cdot}75 \times 10^{-15}$	(1)	
$X^+ + X \rightarrow X + X^+$	$He^+ + He \rightarrow He + He^+$	0·1	$3{\cdot}61 \times 10^{-15}$	(1)	
		1·0	$2{\cdot}90 \times 10^{-15}$	(1)	
	$Ne^+ + Ne \rightarrow Ne + Ne^+$	0·1	$4{\cdot}14 \times 10^{-15}$	(1)	
		1·0	$3{\cdot}34 \times 10^{-15}$	(1)	
	$O^+ + O \rightarrow O + O^+$	0·1	$1{\cdot}00 \times 10^{-14}$	(1)	Not definite.
		1·0	$8{\cdot}8 \times 10^{-14}$	(1)	
	$O_2^+ + O_2 \rightarrow O_2 + O_2^+$	Thermal energy	$\sim 10^{-14}$.	(2)	
	$N_2^+ + N_2 \rightarrow N_2 + N_2^+$	,,	$\sim 10^{-14}$	(2)	
Asymmetric resonance charge transfer	$O^+ + H \rightarrow O + H^+$	20 *eV*	12×10^{-16}	(3)	Experimental.
		90 *eV*	8×10^{-16}	(3)	
$X^+ + Y \rightarrow X + Y^+$	$N^+ + H \rightarrow N + H^+$	20 *eV*	3×10^{-16}	(3)	
$\Delta E \sim O$		100 *eV*	10×10^{-16}	(3)	
	$O^+(^2D) + N_2 (X\ ^1\Sigma_g^+ v = 0)$				
	$\rightarrow O(^3P) + N_2^+ (A\ ^2\pi_u v = 1)$	Thermal energy	Large cross-section improbable	(4)	
Mutual neutralization	$H^- + H^+ \rightarrow H + H$	1/2 – 7	$T^{-1/2}\ 10^7\ cm^3.sec^{-1}$	(5)	T is the absolute temperature.
$X^+ + Y^- \rightarrow X + Y$	$O^+ + O^- \rightarrow O + O$	Thermal energy	$\sim 10^{-8}\ cm^3.sec^{-1}$	(6)	

	$I^+ + I^- \rightarrow I + I$	Thermal energy	$1{\cdot}47 \times 10^{-8}$ cm^3 sec^{-1}	(7)	Experimental.
	$B_r^+ + B_r^- \rightarrow B_r + B_r$	,,	$1{\cdot}85 \times 10^{-8}$ cm^3 sec^{-1}	(7)	,,
Three-body ionic recombination $X^+ + Y^- + M \rightarrow$ $X + Y + M$	atmospheric ions	Thermal energy	$\frac{8 \times 10^{-3}.P}{T^{5/2}}$ cm^3.sec^{-1}	(8), (9), (10) and (11)	P – the pressure in mm. Hg. T – absolute temperature.
		B. High Energy			
Asymmetric non resonance change exchange $X^+ + Y \rightarrow X + Y^+$ Δ	$O^+ + N_2 \rightarrow N_2^+ + O$	20 to 250	$3{\cdot}5 \times 10^{-16}$	(12)	Experimental.
	$N^+ + N_2 \rightarrow N_2^+ + N$	,,	$0{\cdot}88 \times 10^{-16}$	(12)	
	$O_2^+ + N_2 \rightarrow N_2^+ + O_2$	,,	$2{\cdot}2 \times 10^{-16}$	(12)	
	$N_2^+ + N_2 \rightarrow N_2^+ + N_2$	,,	$1{\cdot}84 - 2{\cdot}5 \times 10^{-15}$	(12)	
	$O^+ + O_2 \rightarrow O_2^+ + O$	,,	$4{\cdot}1 - 6{\cdot}2 \times 10^{-16}$	(12)	
	$N^+ + O_2 \rightarrow O_2^+ + N$	,,	$8{\cdot}8 \times 10^{-16}$	(12)	
	$O_2^+ + O_2 \rightarrow O_2 + O_2^+$	,,	$1{\cdot}1 \times 10^{-15} - 8{\cdot}8 \times 10^{-16}$	(12)	
	$N_2^+ + O_2 \rightarrow O_2^+ + N_2$	,,	$4{\cdot}1 \times 10^{-16}$	(12)	
	$O^+ + H_2O \rightarrow H_2O^+ + O$	,,	$9{\cdot}7 - 5{\cdot}3 \times 10^{-16}$	(13)	

(1) Dalgarno, 1985*b* (2) Varney, 1953. (3) Fite *et al*, 1960. (4) Bates and Lynn, 1959. (5) Bates and Lewis, 1955. (6) Dalgarno, 1961. 7) Yeung, 1958 (8) Thompson, 1924. (9) Möchler, 1936. (10) Sayers, 1938. (11) Gardner, 1938. (12) Porter, 1954. (13) Hasted, 1952.

TABLE X

Exchange of atoms and ions

Process	Reaction	Coefficient k	Reference
Two-body process	$N + O_2 \rightarrow NO + O$	$10^{-16} \pm 0{\cdot}02$ cm^3/sec	(1)
	$NO_2 + O \rightarrow NO + O_2$	4×10^{-12} cm^3/sec	(2)
	$N + NO_2 \rightarrow NO + NO$	5×10^{-14} cm^3/sec	(1)
	$N + NO_2 \rightarrow N_2O + O$	$3{\cdot}2 \pm 0{\cdot}5 \times 10^{-14}$ cm^3/sec	(1)
	$N + NO_2 \rightarrow N_2 + O_2$	$2 \pm 0{\cdot}5 \times 10^{-14}$ cm^3/sec	(1)
	$NO + N \rightarrow N_2 + O$	10^{-12} cm^3/sec	(3)
	$NO + O_3 \rightarrow NO_2 + O_2$	$7{\cdot}5 \times 10^{-14}$ cm^3/sec	(3)
	$O + O_3 \rightarrow O_2 + O_2$	5×10^{-11} cm^3/sec	(3)
Two-body radiative association	$O + O \rightarrow O_2 + h\nu$		(3)
	$N + N \rightarrow N_2 + h\nu$		(3)
	$O + NO \rightarrow NO_2 + h\nu$	2×10^{-16} cm^3/sec	(1)
	$N_2 + O \rightarrow N_2O + h\nu$	10^{-30} cm^3/sec	

Three-body process	$NO + NO + O_2 \rightarrow 2NO_2$	10^{-37} cm^6/sec	(1)
	$O + O + M \rightarrow O_2 + M$	5×10^{-34} cm^6/sec	(1)
	$N + O + M \rightarrow NO + M$	5×10^{-32} cm^6/sec	(1)
	$N + N + M \rightarrow N_2 + M$	5×10^{-33} cm^6/sec	(1)
	$N_2 + O + M \rightarrow N_2O + M$	10^{-41} cm^6/sec	(1)
	$O + O_2 + M \rightarrow O_3 + M$	5×10^{-36} cm^6/sec	(3)
Ion-atom interchange	$O^+ + N_2 \rightarrow NO^+ + N$	2×10^{-13} cm^3/sec	(4)
	$O^+ + O_2 \rightarrow O_2^+ + O$	7×10^{-11} cm^3/sec	(4)
	$N^+ + O_2 \rightarrow NO^+ + O$	$1{\cdot}26 \times 10^{-12}$ cm^3/sec	(4)
	$N^+ + O_2 \rightarrow NO + O^+$	$2{\cdot}8 \times 10^{-12}$ cm^3/sec	(4)
	$O_2^+ + N \rightarrow NO^+ + O$	5×10^{-13} cm^3/sec	(4)
	$O_2^+ + N_2 \rightarrow NO^+ + NO$	$2{\cdot}5 \times 10^{-14}$ cm^3/sec	(4)
	$N_2^+ + O \rightarrow NO^+ + N$	$1{\cdot}46 \times 10^{-11}$ cm^3/sec	(4)
	$N_2^+ + N \rightarrow N_2 + N^+$	$1{\cdot}46 \times 10^{-11}$ cm^3/sec	(4)
	$N_2^+ + O_2 \rightarrow NO^+ + NO$	$1{\cdot}46 \times 10^{-11}$ cm^3/sec	(4)

1. Harteck *et el*, 1959. 2. Kristiakowsky *et el*, 1957.
3. Nicolet *et el*, 1958. 4. Ghosh *et al*, 1962.

$$D(XY) \geq D(YO) + E(O^1S)$$

where, D(XY) and D(YO) are the dissociation energies of XY and YO molecules respectively and E(O^1S) is the excitation energy of OI (^1S) atoms.

To obtain the minimum value of D(XY), it should be noted that of all diatomic oxides present at 100 km altitude, OH has the minimum dissociation energy. Substituting D(OH) = 4·36 eV and E(O^1S) = 4·1 eV, we have

$$D(HX) = 4{\cdot}36 + 4{\cdot}1 = 8{\cdot}46\ eV.$$

A hydride of such high dissociation energy is not known to be present at the altitude of 100 km. Thus bimolecular process involving neutral Particle cannot be a possible mechanism for the excitation of λ5577 line in the night airglow.

A bimolecular reaction involving ions cannot also be considered as a possible process because the available energy for the reaction is much larger than the excitation energy of an OI (^1S) atom, and hence the probability of the reaction is low. Also, from the low concentration of ions at 100 km, it can be shown by a simple calculation that the observed rate of emission of λ5577 cannot be obtained by this type of reaction.

Regarding the third type of reaction, it should be noted that the following reaction can only give the observed emission rate.

$$O + O + O \rightarrow O_2 + O(^1S)$$

This is the famous Chapman's reaction. The coincidence of the altitude of maximum rate of λ5577 emission with that of the maximum oxygen atom concentration gives added support in favour of this reaction (Fig. 5).

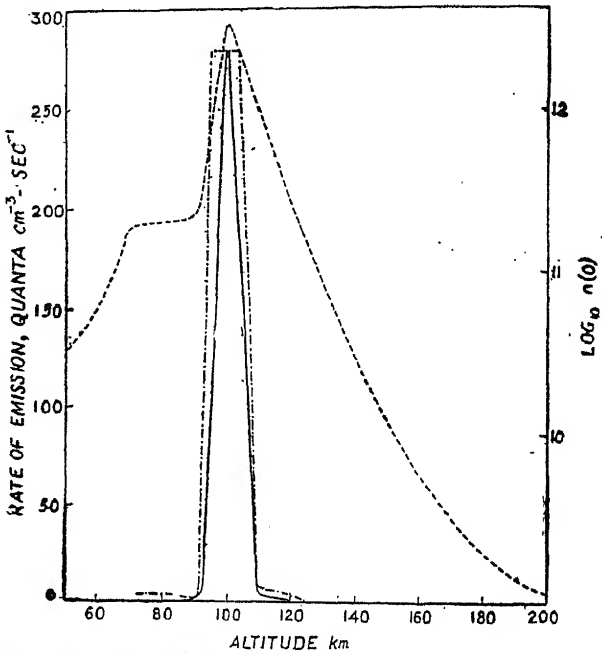

Fig. 5. Variation of rates of emission of 5577 with altitude in the night airglow, (dash – dot curve is given by Heppner and Meredith, 1958 ; full line curve is the calculated one). The distribution of oxygen as given by Miller (1957) is also shown in the same figure (dash curve).

Since λ_{5577} line in the night airglow originates from altitudes around 100 km (Heppner and Meredith, 1958), the region between 50 and 200 km has been selected for the study of the quenching of O(^{1}S) atoms in the upper atmosphere Considering the composition of atmosphere in the above region and values of the rate coefficient of reactions responsible for the quenching, it can be concluded (Ghosh and Sharma, 1961) that reactions responsible for the quenching of OI(^{1}S) atoms are as follows:

$$O^* + O_2(^3\Sigma_g^-) \rightarrow O + O_2(^1\Sigma_g^+, {}^1\Delta_g) \quad (4)$$

$$O^* + (N_2, O_2) \rightarrow O + (N_2, O_2 \text{ vib. excited}) \quad (5)$$

$$O^* + O_2 \rightarrow O_2' + O \quad (6)$$

$$O^* + N_2 \rightarrow NO' + N \quad (7)$$

(In reaction (6), it may be considered that O_2 molecules are at first broken up into two O atoms, one of these atoms combines with O* forming an O_2' molecules).

No precise information regarding the quenching cross-section involving metastable atoms is available. However, according to Laidler (1954), the coefficient of quenching reactions involving non-metastable atoms is of the order of 10^{-12} cm^3/sec. Assuming that the coefficient of quenching of metastable OI(^{1}S) atoms by N_2 and O_2 molecules is one order smaller than the above value, the probability of quenching of OI(^{1}S) atoms, P_q is given by,

$$P_q = [n(O_2) + n(N_2)] \times 10^{-13} \text{ sec}^{-1}$$

where, $n(O_2)$ and $n(N_2)$ are the concentrations of O_2 and N_2 molecules. Assuming the concentrations of atmospheric constituents given by Miller (1957), the altitude variation of P_q is computed and plotted in Fig. 6.

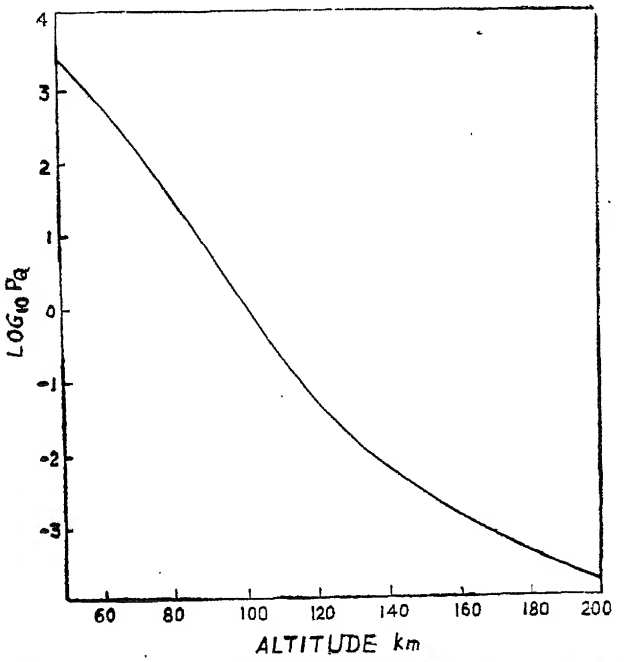

Fig. 6. Variation of quenching probability P_q 5577 with altitude.

Fig. 6 shows the probability of quenching of OI(^{1}S) atoms between altitudes 50 and 200 km. It may be recalled that the altitude variation of the concentration of O atoms given by Miller (1957) and of the emission rate of λ5577 line in the night airglow are plotted in Fig. 5. An examination of Figs. 5 and 6 reveals the following facts.

1. The altitude of the maximum rate of λ5577 emission coincides with that of the maximum oxygen atom concentration, indicating that the process for the excitation of the λ5577 line in the night airglow involves oxygen atoms in the ground state.

2. The quenching probability and the transition probability of $^1S \rightarrow {}^1D$ OI transition are of the same order of magnitude.

From rocket-borne experiments, Heppner and Meredith (1958) showed that the rate of emission of λ5577 at 100 km is 280 quanta cm^{-3} sec^{-1}. Therefore,

$$n(O^1S) \times A_{5577} = 280$$

Where, A_{5577} is the probability of transition from ^1S to ^1D state and $n(O^1S)$ is the concentration of $O(^1S)$ atoms at 100 km. Assuming the value of A_{5577} given by Aller (1953) namely 1·28 sec^{-1}, and the probability of quenching of $O_i(^1S)$ atoms at 100 km 1·3 sec^{-1}, it can be shown that the total rate of de-excitation is given by,

rate of emission + rate of quenching = 280 + 284·4 = 564·4 cm^{-3} sec^{-1} which at equilibrium condition is the rate of production of $OI(^1S)$ atoms.

If the rate coefficient of Chapman's process is k_1, then at the equlibrium condition,

$$n(O)^3_{100} \times k_1 = 564{\cdot}4$$

where $n(O)_{100}$ is the concentration of oxygen atoms at 100 km. Substituting the value of $n(O)_{100}$, we obtain,

$$k_1 = \frac{564{\cdot}4}{3{\cdot}4^3} \times 10^{-36} \text{ sec}^{-1}$$

$$= 1{\cdot}44 \times 10^{-35} \text{ cm}^6 \text{ sec}^{-1}$$

This is a plausible value of k_1 for a three-body reaction.

To determine the variation of emission rate with altitude, let us consider the equlibrium condition of production and destruction of $O(^1S)$ atoms,

$$n(O)^3 . k_1 = n(O^1S) \times [A_{5577} + n(M).k_3]$$

where, k_3 is the rate coefficient of the quenching reaction discussed above. Since the effective quenchers are N_2 and O_2 molecules, $n(M)$ is equal to the sum of the concentrations of N_2 and O_2 molecules. Therefore,

$$n(O^1S) = \frac{n(O)^3 . k_1}{A_{5577} + n(M).k_3}$$

and the emission rate

$$r_{5577} = n(O^1S) \cdot A_{5577} = \frac{n(O)^3 \cdot k_1}{A_{5577} + n(M) \cdot k_3} \times A_{5577} .$$

Substituting the values of k_1 and k_3 and the values of $n(O)$ and $n(M)$ at different altitudes the variation of the emission rate with altitude is computed and is plotted in Fig. 6. It can be seen from this figure that the agreement between the theoretical and experimental values is good.

(ii) EXCITATION OF RED OXYGEN LINES

After emitting the green λ 5577 line, an oxygen atom arrives at the ^1D state. A transition from the former state to the ground ^3P level results in the emission of the red λ 6300 line. Therefore, after emitting the λ 5557 line by radiative transition, an oxygen atom can emit the red auroral line. However, to explain the relative intensity of green and red lines observed in the night airglow, Roach (1954) showed that one has to consider the production of OI (^1D) atoms by some other mechanism in addition to those produced by radiative transition from the ^1S state. A search for such a mechanism can be made in the light of the following observations:

1. *Height of emission of the red* OI *line.* From rocket measurements of the altitude of night airglow emission. Heppner and Meredith (1958) concluded that the emission of OI red lines in the night airglow originates primarily above 160 km although they do not exclude the possibility of emission at lower altitudes, which if it occurs could be only a fraction of the total emission.

2. *Rate of emission.* According to Roach's (1954) observations, the average rate of emission of the red oxygen line in the night airglow is 15×10^6 quanta/cm^2 column.

Assuming Chapman's mechanism for the excitation of the OI red line in the night airglow, namely,

$$O + O + O = O_2 + O\ (^1D) \qquad (8)$$

we can calculate the rate of emission of red lines at different altitudes between 50 and 200 km in the following manner. At equilibrium condition

$$n\ (O^1S).\ A_{5577} + n\ (O)^3.\ k_1' = n\ (O^1D).\ (A_{6300} + P_{q^{6300}}) \qquad (9)$$

where

$n\ (O^1S)$ = concentration of OI (^1S) atoms.

$n\ (O^1D)$ = concentration of OI (^1D) atoms.

A_{6300} = transition probability of the ren OI line.

$P_{q^{6300}}$ = quenching probability of OI (^1D) atoms.

k'_1 = rate coefficient of reaction (8).

The rate of emission of red oxygen line is given by

$$r_{6300} = n\,(O^1D).\,A_{6300}$$

Substituting the value of $n\,(O^1D)$ from (21), we have

$$r_{6300} = \frac{A_{6300}}{A_{6300} + P_{q^{6300}}} \times \left[n\,(O)^3.\,k_1' + \frac{n\,(O)^3.\,k_1.\,A_{5577}}{A_{5577} + P_{q^{5577}}} \right]$$

and assuming $k_1' = \alpha k_1$, $P_{q^{6300}} = \beta\, P_{q^{5577}}$, we have

$$r_{6300} = \frac{n\,(O)^3.\,k_1.\,A_{6300}}{A_{6300} + \beta\, P_{q^{5577}}} \times \left[\alpha + \frac{A_{5577}}{A_{5577} + P_{q^{5577}}} \right]$$

where α and β are constants. Using this formula the relative variation of r_{6300} with altitude can be obtained. However, since the values of α and β are not precisely known and the value of k_1 is uncertain, a quantitative estimate of the variation of r_{6300} with altitude cannot be made. A rough estimate of this variation can be made in the following way. Depending on the values of $P_{q^{6300}}$ and $P_{q^{5577}}$ as estimated by Seaton (1958), the upper region of the atmosphere is divided into three regions.

I. *Lower region.* This region is situated below 100 km altitude, where the following condition exists:

$$P_{q^{5577}} >> A_{5577}, \text{ and } P_{q^{6300}} >> A_{6300}.$$

In this region, the rate of emission of the red OI triplet is given by

$$r_{6300} = \frac{n\,(O)^3.\,k_1.\,A_{6300}}{\beta\, P_{q^{5577}}} \times \left[\alpha + \frac{A_{5577}}{P_{q^{5577}}} \right]$$

when the oxygen atom concentration increases and $P_{q^{5577}}$ decreases with the altitude (see Fig. 5). Therefore, r_{6300} rapidly increases up to 100 km altitude.

II. *Middle region.* This region is situated above 100 km and extends to 200 km, where the following condition holds, namely

$$P_{q^{5577}} << A_{5577} \text{ and } P_{q^{6300}} >> A_{6300}.$$

Consquently, r_{6300} is given by

$$r_{6300} = \frac{n\,(O)^3.\,k_1.\,A_{6300}}{\beta\, P_{q^{5577}}} \times (\alpha + 1).$$

In this region the altitude variations of r_{6300} is given by

$$\frac{\triangle r_{6300}}{\triangle h} = r_{6300} \times \left[\frac{3.\triangle n\,(O)}{n\,(O).\triangle h} - \frac{\triangle n\,(M)}{n\,(M).\triangle b} \right]$$

where h represents the altitude of emission and n (M) the sum of concentration of O_2 and N_2 molecules. From the distributions of O, O_2 and N_2 given by Miller (1957), it is found from the above relation that in this region $\Delta r_{6300} / \Delta h$ is negative, i. e. the rate of emission decreases with altitude.

III. *Upper region.* This region is located above 200 km. In this region the following condition exist:

$$P_{q^{5577}} << A_{5577}, \text{ and } P_{q^{6300}} << A_{6300}$$

and therefore the rate of emission of the 6300 line is given by

$$r_{6300} = n\,(O)^3.\, k_1.\, (\alpha + 1).$$

Since in this region the concentration of oxygen atoms decreases with altitude, the rate of emission also decreases. Therefore, it can be concluded that if the emission of the λ 6300 line in the night airglow is also due to Chapman process, the maximum rate of its emission should occur at about 100 km where the atomic oxygen concentration is a maximum. As this is contrary to observations, we may conclude that the process responsible for the emission of the λ6300 line is different from that by which the green line is emitted. This conclusion is supported by the fact that the seasonal and diurnal variations of the intensity of the green line are markedly different from those of the red OI line (Roach, 1954).

Considering the other processes mentioned in Section 4*i*, it should be noted that at altitudes higher than 160 km, the rate of any tri-molecular process is too low to explain the observed emission.

If a bimolecular process involving neutral particles could emit the λ 6300 line, it should be of the following type:

$$X + YO = XY + O\,(^1D).$$

For this process to be valid, the following condition should hold (see Section 4*i*):

$$D\,(XY) - D\,(YO) > E\,(O^1D)$$

where E (O^1D) is the excitation energy of O^1D atoms, which is 1·96 eV. Above 160 km, the only possible reaction of the above type is given by

$$N + NO = N_2 + O\,(^1D) \qquad (10)$$

because

$$D\,(N_2)\,(9{\cdot}76\text{ eV}) - D\,(NO)\,(6{\cdot}48\text{ eV}) = 3{\cdot}28\text{ eV} > E\,(O^1D).$$

At equilibrium condition, we have

$$n\,(N).\, n\,(NO).\quad k_4 = n\,(O^1D).\, (A_{6300} + P_{q^{6300}})$$

where n (N), n (NO), and n (O^1D) are respectively the concentrations of N, NO and O^1D and k_4 is the rate coefficient of reaction (10). Therefore, according to the above process, the rate of emission of the red oxygen line in the night airglow is given by

$$r_{6300} = n\,(O^1D).\, A_{6300}$$

$$= \frac{n\,(N).\, n\,(N)\,.\, k_4}{A_{6300} + P_{q^{6300}}} \times A_{6300}.$$

In the region around 100 km, the magnitude of P_{q6300} is much larger than A_{6300}. ad therefore $r_{6300}$is given by

$$r_{6300} = \frac{n\,(\mathrm{N}).\ n\,(\mathrm{NO}).\ k_4}{P_{q6300}} \times A_{6300}.$$

Using the distribution of N and NO given by Miller (1957) and the value of P_{q6300} given by Seaton (1958), one finds that λ 6800 line should be emitted at about 100 km (contrary to observation) and that the rate of emission be decreased with altitude, which is also contrary to observations. Hence, it can be concluded that the above process is not responsible for the emission of the red oxygen line in the night airglow. It may contribute a small fraction of this emission at lower altitudes as reported by Heppner and Meredith(1958).

It is to be noted that because of the low concentration of negative ions, the λ 6300 line cannot be emitted by mutual neutralization of positive and negative ions. Also, radiative recombination between O^+ + and e is not a plausible reaction as its coefficient (Bates *et al*, 1939) and the concentrations of ions and electrons are very low.

As regards the dissociative recombination process, it may be noted that Bates (1956) has shown that the following reaction can only account for the observed high recombination coefficient in the F-layer.

$$O_2^+ + e = O' + O'$$

where dash signifies excited atoms. Assuming that either one or both oxygen atoms are excited to ^1D level, one finds that at equilibrium condition, the following relation holds:

$$b.n\,(O_2^+),\ n\,(e).\ \alpha = n\ (O^1D)\ (A_{6300} + P_{q6300})$$

where α is the rate coefficient of the above process, and b may have a value of 1 or 2 depending on whether one or both atoms are excited. The rate of excitation of the red OI line is then given by

$$r_{6300} = \frac{b.\ n\,(O_2^+)\ n\,(e)\ \alpha}{A_{6300} + P_{q6300}} \times A_{6300}$$

Since, in the region above 160 km

$$P_{q6300} << A_{6300}$$

we have

$$r_{6300} = bn\,(O_2^+).\ n\,(e).\ \alpha$$

Substituting the value of α which is of the order of 10^{-7} cm sec^{-1} (Bates, 1950) and the value of the electron density given by Jackson and Seddond (1958) and putting $b = 1$ in the above equation, it is found that the observe rate of emission can be explained if the concentration of O_2^+ is 5×10^3 ions cm^{-3}. This is the expected (Bates, 1956) concentration of O_2^+ ions in the F-region of the ionosphere. It may be noted that by assuming the above process, Chamber-

lain (1958) explained the observed rate of decrease of r_{6300} after sunset at the altitude of emitting layer. Moreover, Barbier (1957) has shown strong correlation between the intensity of λ 6300 line in the night airglow with the critical frequency and the height for vertical reflexion of radio waves from the F-region of the ionosphere. Also, St. Amand (1955) has established a definite correlation between the intensity of λ 6300 line with F-layer ionization. Hence, it can be concluded that the most probable mechanism for the excitation of the red oxygen line in the night airglow is the dissociative recombination of molecular oxygen ions with electrons.

(*iii*) EXCITATION OF Na-D LINES IN THE NIGHT AIRGLOW

Any proposed mechanism for the excitation of λ 5893 line in the night airglow should explain the following observed facts (Heppner and Meredith, 1958),

1. That the D-lines of Na are emitted around an altitude of 95 km with maximum emission at 93 $\pm$ 3 km, and
2. That the emission rate is about 150 quanta cm^{-3} sec^{-1}.

Considering the composition of the upper atmosphere at about 95 km where the yellow D-line is emitted, λ 5893 line may be produced also by a reaction of the type given in Section 4*i*. In addition to the above reactions the following process should also be considered.

(*d*) The transfer of energy during collision :

The Chapman's process (1939), which is of the type (a) (Sec. 4*i*) for the emission of D-lines in the night airglow is as follows.

$$NaO + O \rightarrow Na^* + O_2 \qquad (11)$$

$$Na^* \rightarrow Na + h\nu \ (\lambda\ 5893)$$

where, NaO molecules are produced by,

$$Na + O_3 \rightarrow NaO + O_2 \qquad (12)$$

Considering the distribution of Na (Barbiex *et al*, 1949) and that of O_3 (Newell, 1953) and assuming that the rate coefficient of the reaction (12) to be $1{\cdot}5 \times 10^{-11}$ cm^3 sec^{-1}, we find that

1. The height of the maximum emission rate should be below 70 km, and
2. The total intensity should be greater than the observed value.
3. If sodium is sprayed from a rocket, the emission should be greater at heights below 70 km than above it.

The above conclusions are in disagreement with the observed facts (Heppner and Meredith, 1958 and Edwards *et al* 1956).

Furthermore, there are several experimental evidences against Chapman's process. For example, it has been shown by Tanaka and Ogawa (1956), that in the range of temperature from 250°C to 450°C, the intensity of D lines is vary weak at 450°C compared to that at 250°C . The decrease in the intensity is attributed to the dissociation of Na_2 molecules at high temperature. The relative

proportion of Na_2 molecules at different temperatures has been calculated by Benton and Inatomi (1952). The proportion of Na_2 varies from 97% at 250°C to 70% and 450°C. From this observation, it can be concluded that Na – O_3 reaction is less efficient in producing chemiluminescence compared to Na_2 – O_3 reaction. Since in the upper atmosphere sodium is present in atomic form a reaction involving O_3 should not be favoured.

Owing to low concentrations, a bimolecular process involving ions and electrons, is too slow to give the observed rate of emission. As regards the three-body reactions, it may be noted that the following type of associative process can produce excited Na atoms:

$$Na + X + Y = Na^* + XY \qquad (13)$$

Assuming the rate coefficient of the above process of the same order as that as similiar processes (Table X) to be 10^{-32} cm^6 sec^{-1} and considering the three-body recombination of O atoms with Na, we find that the rate of excitation of Na atom is about 10^{-4} cm^{-3} sec^{-1}. Therefore, at the altitude of emission of D-lines, a three-body reaction can not also explain the observed rate of emission.

The transfer of energy during collision from one particle to Na should be of the following type:

$$Na + XY' \rightarrow Na^* + XY \qquad (14)$$

It may be recalled that the transfer of vibrational energy to electronic excitation energy has been suggested by several workers. Polyani (1932), for the first time suggested the excitation of Na atoms by vibrationally excited NaCl molocules. Gaydon and Wolfhard (1950) also suggested electronic excitation of C_5 by vibrationally excited C_2 molecules. Summarising various evidences, Laidler and Shuler (1951) concluded that such energy transfer is favoured when the energy of eleetronic state is low. Assuming the rate coefficient of the process (14) to be about, 10^{-12} cm^3 sec^{-1} (Laidler, 1954), the rate of excitation of Na is given by,

$$n(\text{Na}).\ n(\text{XY}') \times 10^{-12}\ \text{cm}^{-3}\ \text{sec}^{-1}$$

and equating with the rate of emission of λ 5893 line in the night airglow, after substituting the concentration of Na atoms of about 10^4 cm^{-3} and 90 km (Barbier et al, 1949) we find that

$$n(\text{XY}') = 1{\cdot}5 \times 10^{10}\ \text{molecules cm}^{-3}$$

Considering the concentration of the atmospherie constituents at altitude of emission, we conclude that vibrationally excited O_2 and N_2 molecules can excite Na atoms. Regarding the presence of the vibrationally excited molecules in the upper atmosphere, it may be noted that they can be produced by any one of the following processes:

$$X + Y \rightarrow XY' + h \qquad (15)$$

$$X + Y + M \rightarrow XY' + M \qquad (16)$$

$$O\ (^1S \text{ or } ^1D) + XY \rightarrow O\ (^3P) + XY' \qquad (17)$$

Moreover, since O_2 and N_2 are homonuclear diatomic molecules, the radiative de-excitation by rotational vibrational transition is not allowed. As indicated by the ultrasonic absorption by these gases (Mott and Massey, 1949), the transfer of vibrational energy of O_2 and N_2 to the translational energy during collisions is not also favoured. Therefore, it may be expected that a large concentration of

vibrationally excited diatomic molecules can be built up in the upper atmosphere. At the altitude of emission, since the rate of dissociation of O_2 is much larger than that of N_2, the concentration of vibrationally excited O_2 produced by the following reactions.

$$O + O \rightarrow O_2' + h\nu$$

$$O + O + \rightarrow O_2' + M$$

should be larger than that of N_2. Therefore, it may be inferred that the most plausible mechanism for the excitation of D-lines in the night airglow is,

$$Na + O_2' \text{ (vib. excited)} \rightarrow Na^* + O_2$$

$$Na^* \rightarrow Na + h\nu \ (\lambda\ 5893).$$

5. IDENTIFICATION OF N ATOMS PRODUCED BY DISSOCIATIVE RECOMBINATION OF N_2^+ WITH ELECTRONS

The dissociative recombination of N_2^+ ions with electrons, namely

$$N_2^+ + e \rightarrow N^* + N^* \qquad (18)$$

is important for several reasons. It plays important role in nitrogen discharge. Also, it is considered to be a process by which N atoms in upper atmosphere may be produced. The other process for the production of N atoms in the upper atmosphere is the predissociation of N_2 molecules, namely

$$N_2 + h\nu \ (\lambda < 1250\ A) \rightarrow N + N \qquad (19)$$

It has not yet been definitely decided which of the above processes plays greater role in the production of N atoms in the upper atmosphere.

Several workers (Biondi and Brown, 1949, Sayers, 1956, Faire *et al*, 1958, Bialecke and Dougal, 1958, Faire and Champion, 1959) have measured the rate coefficient of the reaction (18) and have found its value between 10^{-6} to 10^{-7} cm^3 sec^{-1}. Recently Ghosh, Sharma and Sharma (1962 a) have found that in order to explain the observed distribution of positive ions in the F-region of the ionosphere, its value should be 4×10^{-7} cm^3 sec^{-1}.

To understand the reaction (18) completely, one should know, in addition to its rate coefficient, the products of the reaction and their states. If we assume the dissociation energy of N_2 molecule to be 9·78 eV as given by Gaydon (1952), the ionisation energy of N_2 is completely balanced if the two N atoms are in states ^2P and ^2D respectively. Normally, under resonance condition, the coefficient of the reaction is expected to be high. However, these states are highly metastable (life times being 2·1 sec for ^2P and 8 hrs for ^2D), and therefore, it is difficult to obtain radiation from these levels in a discharge tube, because walls of the discharge tube kill the metastable atoms. Consequently, attempts made by several workers to identify the states of the resultant N atoms have proved to be fruitless.

It is proposed here that the reaction products can be identified, if the dissociated N atoms are irradiated by ultraviolet rediation so that they are raised to higher non-metastable states and then observing the ensuing flouresccnce.

In fig. 7 the energy level diagram of NI is shown. The allowed transition from the ground ^4S and from the metastable ^2D and ^2P states are shown in Fig. 7.

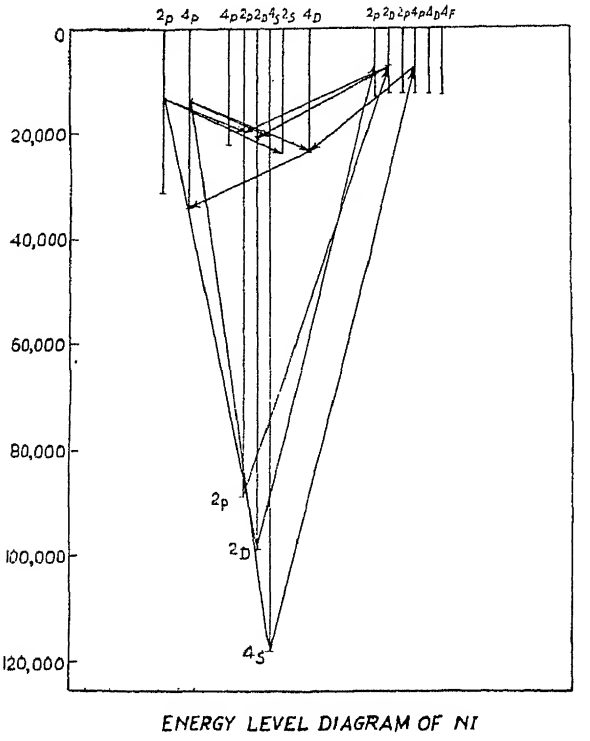

Fig. 7. Energy level diagram of NI showing some allowed transitions.

It may be seen that the wavelength of absorbing radiation for the allowed transitions lie in the vacuum ultraviolet region. The wavelengths of the ensuing flourescent radiation given in Table XI, which shows that the presence of normal ^4S can be identidied by the presence of λ 6431 line in the flourescence spectrum. If, however, N atoms are formed in ^2P and ^2D states as a result of the dissociation of N_2^+ ions with electrons, the flourescence spectra should show another line at 6000 A, which falls in the visible region and therefore can be easily observed.

We can therefore, conclude that for the identification of the states of N atoms produced as a result of disociative recombination of N_2^+ with electrons, the exciting and flourescent radiations should be as given in Table XI.

TABLE XI

State of N atoms	Wavelength of exciting radiation (A)	Wavelength of fluorescent radiation (A)
^4S	965 – 906	6431
^2D	1008 — 1177	6000
^2P	1320 — 1228	6000

It may be pointed out that the exciting radiation can be isolated by a vacuum ultraviolet monochrometor from the light obtained from N_2 spark.

6. SPECTRA EXCITED BY ION BOMBARDMENT

The excitation of spectra by ion bombardment, in particular by protons has, of late, been receiving increasing attention. This is mainly due to the fact that protons emanated from the sun excite at least a part of the auroral spectra. Ghosh and Srivastava (1962) have extensively reviewed the excitation of spectra by ion bombardment. We shall here consider the mechanism of the excitation of spectra by proton bombardment.

The characteristics of the spectra excited by protons of different energies are collected in table XII,

TABLE XII

Characteristics of Spectra Excited by Proton Bombardment

Proton Energy (Kev)	Bombarded gas	Gas pressure (mm Hg)	Excited spectra	Reference
230	air	0·3	N_2^+ (1N), H_β, N_2 (2P)	(1)
40-230	air	0·3	N_2^+ (1N), NII, H_α, H_β H_γ, N_2 (1P, 2P)	(2)
5-350	air	(1-0·1) × 10^3	N_2^+ (1N), N_2 (2P), NII NI, N_2 (1P), N_2^+ (Meinel) H_α, H_β, H_γ	(3)
5-350	air	,,	N_2^+ (Meinel), N_2^+ (1N) N_2 (1P, 2P), OI, NI, NII O_2 (1N), H_α, H_β, H_γ	(4)
	N_2	8-150	N_2 (2P), N_2^+ (1N, 0-0)	(5)

[666]

100-150	air	few mm	N_2 (2P), N_2^+ (1N)	(6)
2	H_2, He	10^{-3}	H_β	(7)
2·4	N_2	$(0{\cdot}5 - 50) \times 10^{-3}$	N_2^+ (1N), N_2 (1P, 2P) N_2^+ (Meinel), NI H_α, H_β, H_γ	(8a, b)
1000	N_2	$(63\text{-}150) \times 10^{-3}$, 5, 25 and 760 mm	N_2^+ (1N), N_2 (1P, 2P) N_2 (G. G)	(9)
500	,,	5 – 20, 0·15	N_2^+ (1N), N_2 (1P, 2P)	(9)
1000	O_2	atmospheric pressure	OI, OII	(9)
500-1000	N_2	$< 0{\cdot}1$	N_2^+ (1N, Meinel) N_2 (1P, 2P), NI and NII	(10)

1N — First negative

1P — First positive

2P — Second positive

G. G.— Green Gaydon systems

HI lines — 8188, 8681 and 8712 A.

NII lines — 5004, 5680 and 6482 A

OI lines — 3947, 3954, 7156, 7254, 7473-80, 7722-75, 7943-52, 7981-99, 8221-35 and 8446-47 A.

OII lines — 4069-76, 4119, 4185-90, 4275, 4277, 4317-19, 4347-51, 4367, 4368, 4415-17, 4465-69, 4590-96, 4641-61, 4699, 4699-705 A.

(1) Meinel and Fan, 1952. (2) Fan and Meinel, 1953. (3) Fan, 1956*a*. (4) Fan, 1956*b*. (5) Shaleck *et al*, 1954. (6) Branscomb *et al*, 1954. (7) Dietrich, 1956. (8*a*) Carleton, 1957. (8*b*) Carleton and Lawrence, 1958. (9) Nicholls *et al*, 1959. (10) Reeves *et al*, 1960.

which shows that the excited spectra are of two types: (a) that of bombarded gas and (b) that due to bombarding ions. Following processes play important role in the excitation of spectra in gases by ion bombardment:

(*i*) Electron exchange with excitation

(*ii*) Electron exchange followed by dissociation and excitation

(*iii*) Ionization with excitation

(*iv*) Ionization followed by dissociation and excitation

(*v*) Mutual neutralization leading to excited atoms and molecules.

The electron exchange processes (i) and (ii) are of the following types:

$$X^+ + YZ \rightarrow X + YZ^+ (\pm \triangle E)$$

$$X^+ + YZ \rightarrow X + Y^+ + Z (\pm \triangle E)$$

where, X^+ is the incident ion and YZ is the molecule of the bombarded gas. The products of the reaction may be in the ground and the excited states.

The above process is of fundamental importance in ion transport phenomena for two reasons, (1) the change in the energy involved in the process is considerably less than that for pure ionization or excitation and (2) negligible kinetic energy transfer takes place between the incident ion and the ion formed by charge exchange. In pure ionization the incident particle must possess an amount of kinetic energy at least equal to the ionization potential of the bombarded particle, in charge exchange the energy change is just the difference between ionization potential of the two particles (assuming them to be in the ground states). Thus, a charge exchange process may occur when the incident ions have very small kinetic energy. It has been shown by Sherwin 1940 and Keene (1949) that ions formed in a charge exchange reaction have much less than 1 volt energiy even when the incident ions are of very high energy. Therefore, the kinetc energy of neutralized ions (atoms formed by charge exchange) is usually much larger than that of charge exchange ions.

For a large number of charge exchange reactions Massey's (1949) adiabatic condition holds, namely

$$a. \triangle E/\hbar V = 1$$

where, a is interaction distance (usually 7 A)

$\triangle E$—Difference between ionization potentials of colliding particles

V—velocity of incident ions.

Fan (1958) has shown that for endothermic reactions, the cross section for charge exchange is maximum for the energy E_0 of the incident ions given by,

$$E_0 = - Q. M/m$$

where, M – mass of the incident ion

m – electronic mass

$Q (< 0)$ – the difference of binding energies of electrons in the two states before and after being transferred.

Nicholls and Pleiter (1956) hold that if, in a charge exchange reaction the time of collision is comparable to the period of internuclear vibration, a violent perturbation of the internuclear motion occurs thereby producing dissociation and electronic excitation. They showed that charge exchange with dissociation becomes predominant if,

$$f = (2M/E)^{1/2} = 0{\cdot}1$$

where, f – number of half periods of internuclear vibrations during which ion crosses the molecular diameter

M – ionic mass in atomic weight units

E – ion energy in eV.

Nicholl and Pletier (1956) contended that for $0{\cdot}001 < f < 0{\cdot}01$, only charge exchange without dissociation) occurs.

Since we are primarily interested in the interactions between protons and atmospheric gases the charge exchange cross-sections for (H^+ – air), (H^+ – N_2) and (H^+ – O_2) are shown in Fig. 8 from 10 eV to 1 MeV ion energies. It will be

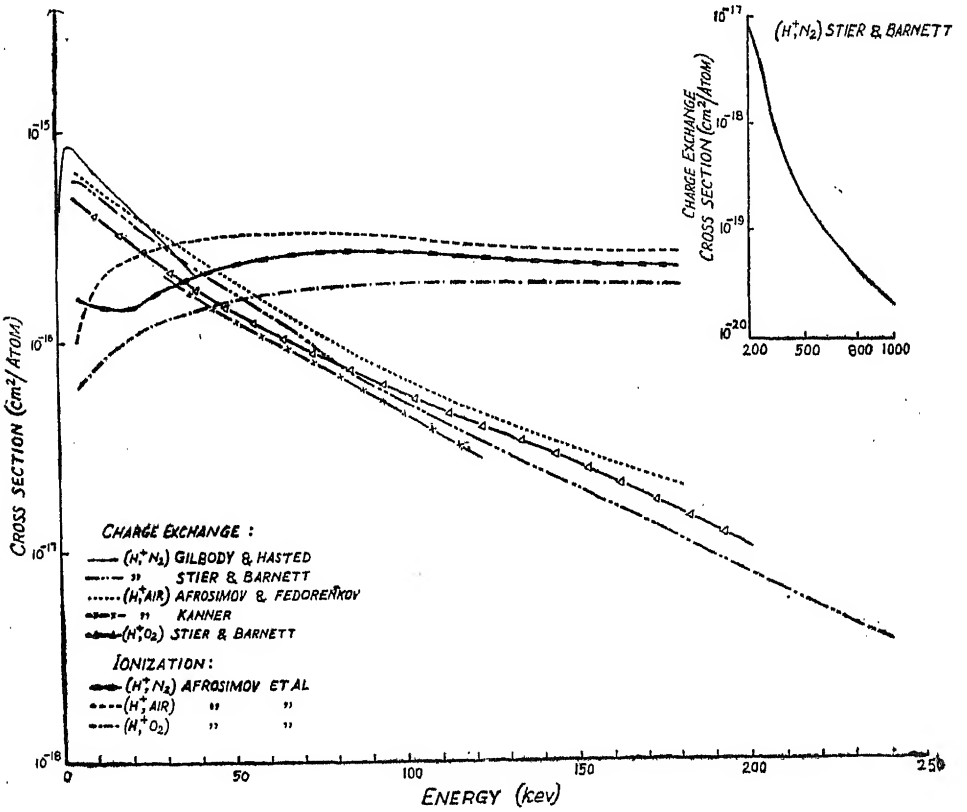

Fig. 8. Charge exchange cross-section for (H+ – air), (H+ – N_2) and (H+ – O_2) from 19 eV to 1 MeV ion energies and the cross-section for ionization.

seen that in the above energy range cross-sections vary over several orders of magnitudes and that they become maximum at few KeV ion energy.

We have seen above that the charge exchange cross-section becomes large at comparatively low energy and decreases rapidly with energy when the energy is of the order of several tens of KeV. In the high energy range, the bombarded particles are ionized and we have the following processes for the interactions between ions and diatomic molecules:

$$X^+ + YZ \rightarrow X^+ + YZ^+ + e$$

$$X^+ + YZ \rightarrow X^+ + Y + Z^+ + e$$

In these cases the reaction products may also be in excited states. The cross-sections for ion zation of N_2, O_2 and air by proton bombardments are shown in Fig. 8, which confirm this statement.

In addition to the above processes the following mutual neutralization processes can also produce excited particles:

$$X^+ + YZ^- \rightarrow X^* + YZ^* \ (\pm \Delta E)$$

$$X^+ + YZ^- \rightarrow X^* + Y^* + Z \ (\pm \Delta E)$$

The ionization energy of X minus the electron affinity of YZ molecule is shared by the neutralized atoms and molecules. Bates and Massey (1946) has shown that near about the resonance condition ($E \simeq O$), the probability of such a reaction is high.

(*a*) *Spectra of the Bombarded Gas*:

The spectra of N_2, O_2 and air bombarded by proton (see Table XII) consists of band systems of N_2^+ (first negative) and (Meinel), band system of N_2 (1st and 2nd Positive), band system of O_2^+ (1st negative), atomic lines (neutral and ionized) of nitrogen and oxygen. No neutral band system of O_2 is observed. We shall now consider the mechanism for excitation of these features separately.

(*i*) N_2^+ 1st *Negative System*:

Fan and Meinel (1952) and Fan (1955) proposed the following reaction for the excitation of this band system:

$$(X^+ \text{ or } e) + N_2 \rightarrow (X \text{ or } e + e) + N_2^{+*} (B^2\Sigma) \quad \text{(charge exchange)}$$

$$(X^+ \text{ or } e) + N_2 \rightarrow (X^+ \text{ or } e) + N_2^{+*} + (B^2\Sigma) + e \quad \text{(ionization and excitation)}$$

where, X^+ is the incident ion and e the secondary electron produced at the walls of the collision chamber by the bombardment of incident ion. After reducing the ejection of secodary electrons Fan (1955) has confirmed the validity of above processes.

From the linear plot of light intensity per unit current of proton with N_2 pressure, Carleton (1957) observed that N_2^+ 1st negative system is excited by a single collision process, namely

$$H^+ + N_2 \rightarrow H + N_2^{+*} \text{ (charge exchange)}$$

$$H^+ + N_2 \rightarrow H^+ + N_2^{+*} + e \text{ (ionization and excitation).}$$

In accordance with the above discussion, charge exchange is favoured at low ion energy bombardments.

The first negative system of N_2^+ can not be excited by secondary bombardments by a two stage process, namely (*a*) production of electrons by bombardment of ions and (b) excitation of 1st negative bands by electrons. The variation of light intensity with N_2 pressure would then be given by a quadratic curve instead of by a linear one.

From the absence of Balmer lines of H atoms in spectra excited by high energy protons in N_2, Nicholls *et al* (1959) concluded that at high energy the charge exchange cross-section is low and hence the first negative bands are excited by,

$$H^+ + N_2 \rightarrow H^+ + N_2^{+*} + e$$

The secondary electrons thus produced may also excite N_2^+ 1st negative. While corroborating the suggestion given by Fan (1956a, 1956 b), Branscomb *et al* (1954) have also suggested that 1st negative system of N_2^+ may also be produced by neutral H atom bombardments.

(*ii*) N_2^+ *Meinel Band System*:

Fan (1956b), after comparing the spectra excited by the bombardment of N_2 by primary and secondary electrons and protons at different energies, has found that the ratio of the intensity of Meinel to 1st negative band system is more or less same for ions as for electrons of the same velocity. However, this ratio is much larger for 300 KeV protons compared to that produced by 20 KeV protons. Moreover for 205 KeV proton bombardments in air, he observed that the ratio of intensity of 1st negative system to Meinel system on N_2^+ is about ten times higher than that produced by electrons with an energy of 120 KeV. This difference, he suggested, is due to the fact that in the case of ion bombardment, there is appreciable momentum transfer, which causes an increase in the internuclear distance of N_2^+ ions after collisions.

From the linearity of the plot between the intensity of N^+ Meinel band per unit current of bombarding particle with N_2 pressure, Carleton (1957) and Carleton *et al* (1958) suggested that the excitation mechanism of the Meinel system may be as follows:

$$H^+ + N_2 \rightarrow H + N_2^{+*}(A^2\pi) \qquad \text{(charge exchange)}$$

$$H^+ + N_2 \rightarrow H^+ + N_2^{+*}(A^2\pi) + e \text{ (ionization and excitation)}$$

At low ion inergy, the charge exchange mechanism is favoured compared to ionization. The observations of Reeves *et al* (1960) also support the above conclusion.

(*iii*) *1st and 2nd System of* N_2 :

The excitation of first and second positive system of N_2 involves a change in multiplicity, therefore the excitation of these systems is attributed to several secondary processes. Fan (1959b) and Nicholls *et al* (1959) observed that N_2 molecules are excited by secondary electrons produced by either the collision between protons and N_2 or from walls by bombardments of ions. On the other hand Shalek *et al* (1954) and Carleton (1957) hold that these band systems are excited by H atoms, produced by the charge exchange between protons and N_2 molecules.

Meinel and Fan (1952) assumed the following processes due to secondary electrons:

$$N_2 + e \rightarrow N_2 (B^3 \pi_g \text{ or } C^3 \pi_u) + e$$

$$N_2^+ + e \rightarrow N_2 (B^3 \pi_g \text{ or } C^3 \pi_u)$$

Fan (1956b) verified the latter process by comparing the spectra excited by 23 eV and 500 eV electrons and 30 KeV protons. When N_2 is bombarded by 23 eV electrons, only 1st and 2nd positive systems are excited, indicating that N_2 molecules are excited by the 2nd process. In the spectra excited by 500 eV electrons and 20 KeV protons, the intensities of 1st and 2nd positive systems of N_2 are negligible, indicating that for high energy electrons and proton bombardment N_2 molecules are ionized and excited.

Carleton (1957) observed that the intensity of 1st positive system of N_2 varies approximately as the square of N_2 pressure, thereby confirming that this system is excited by secondary process. He holds that the 1st positive system of N_2 is produced by neutral H atoms formed by charge exchange between protons and N_2 Molecules. Bates (1954) has corroborated the view that N_2 1st and 2nd positive systems are excited by high energy H atoms produced by the charge exchange of bombarding proton with N_2 or by the capture of secondary electron by the proton.

(*iv*) *Atomic Nitrogen Lines*:

Excitation of these lines may be produced by the following reactions:

$X^+ + N_2 \rightarrow X + N^{+*} + N^*$ (Charge exchange followed by dissociation and excitation)

$X^+ + N_2 \rightarrow X^+ + N^{+*} + N + e$ (Ionization followed by dissociation and excitation)

It may be noted that the former process is operative at low ion energy and the latter at high ion inergy.

(*v*) O_2^+ *Ist Negative*, OI *and* OII *lines*:

Fan (1956b) suggested that O_2^+ 1st negative system is excited by secondary electrons produced either from walls or by reaction between ions and the bombarded molecules.

Nicholls *et al* (1959) suggested following mechanism for the excitation of OI and O I lines excited by bombardment of 1 Mev protons in oxygen at atmospheric pressure:

$H^+ + O_2 \rightarrow H^+ + O^{+*} + O^* + e$ (ionization followed by dissociation and excitation)

It is to be noted that Balmer lines of H atoms are not excited by high energy proton bombardment of O_2 indicating that charge exchange does not occur.

(*vi*) HI *lines*:

Meinel and Fan (1952) and Carleton (1957) observed Balmer lines in the spectra excited by bombardment of air or N_2 with protons, together with Doppler

shifted Balmer lines. They have suggested following mechanism for excitation:

$H^+ + YZ \rightarrow H^* + YZ^+$ (charge exchange giving Doppler shifted lines)

$H^+ + YZ \rightarrow H^* + YZ^{+*}$ (charge exchange followed by excitation of ions giving Balmer lines.)

7. ION-ATOM INTERCHANGE REACTION AND DISTRIBUTION OF POSITIVE IONS IN F-REGION

Following processes together with the diffusion of ions and electrons are controlling the distribution of ions in the ionosphere :

i. Photoionization of the atmospheric constituents,

ii. ion-atom interchange, and

iii. dissociative recombination of molecular ions with electrons.

With the exception of the ion-atom interchange reactions, the rate coefficients of the above processes are known. In this section, from the rocket-borne experimental determination (Johnson, 1961) of the percentage of ion composition upto 220 km, the rate coefficients of ion-atom reactions are obtained. Using these rate coefficients, the ion distribution in the F-region are calculated upto 400 km. It is found that above 180 km, diffussion and ion drift must be taken into account to obtain the correct ion distribution with height.

Daytime Ionospheric processes :

The ionization of the upper atmospheric particles, which consists mainly of O_2, N_2, O, N and NO, is caused by solar radiation in the X-ray and ultraviolet regions. Rates of production of ions by X-ray have been calculated by Ghosh and Sharma (1961*a*). In addition to ionization by X-rays, Ghosh and Sharda Nand (1960, 1962) considered ionization by ultraviolet radiations and those produced by Auger electrons and photoelectrons.

Bates (1955) showed that primary photo-ions are reshuffled by the ion-atom interchange process. To obtain daytime ion distribution in the F-region, consider the possible ion-atom interchange reactions as given by Hertzberg (1961), namely,

$$
\begin{aligned}
&O^+ + N_2 \rightarrow N'^+ + N + (1{\cdot}114 \text{ eV}) && (i)\\
&O^+ + O_2 \rightarrow O_2^+ + O + (1{\cdot}53 \text{ eV}) && (ii)\\
&N^+ + O_2 \rightarrow NO^+ + O + (6{\cdot}70 \text{ eV}) && (iii)\\
&N^+ + O_2 \rightarrow NO + O^+ + (2{\cdot}32 \text{ eV}) && (iv)\\
&O_2^+ + N \rightarrow NO^+ + O + (4{\cdot}23 \text{ eV}) && (v)\\
&O_2^+ + N_2 \rightarrow NO^+ + NO + (0{\cdot}99 \text{ eV}) && (vi)\\
&N_2^+ + O \rightarrow NO^+ + N + (3{\cdot}10 \text{ eV}) && (vii)\\
&N_2^+ + N \rightarrow N^+ + N_2 + (1{\cdot}04 \text{ eV}) && (viii)\\
&N_2^+ + O_2 \rightarrow NO^+ + NO + (4{\cdot}50 \text{ eV}) && (ix)
\end{aligned}
\qquad (20)
$$

The reaction $O_2^+ + N \rightarrow NO + O^+$ which has been considered by Hertzberg has been neglected in our analysis as the reaction is endothermic (Bates and Nicolet, 1961).

The following recombination reactions are considered :

$$O_2^+ + e \rightarrow O' + O' \quad (i)$$
$$N_2^+ + e \rightarrow N' + N' \quad (ii) \qquad (21)$$
$$NO^+ + e \rightarrow N' + O' \quad (iii)$$

where ($'$) signifies excited species. Due to the high rate of photodissociation of negative ions, its presence has been neglected for considering the daytime equilibrium of positive ions.

The equations governing the daytime distribution of positive ions in the F-region are given by,

$$\dot{N} = J_1 a + J_2 b + J_3 c + J_4 d + J_5 e - N(\beta_1 x_1 + \beta_2 x_2 + \beta_3 x_5)$$
$$= q - N(\beta_1 x_1 + \beta_2 x_2 + \beta_3 x_5)$$

where, $n(O_2)$, $n(N_2)$, $n(O)$, $n'N$) and $n(NO)$ are denoted by a, b, c, d, and e respectively. $n(O^+)$, $n(N_2^+)$, $n(O^+)$, $n(NO^+)$, and $n(e)$ are represented by x_1, x_2, x_3, x_4, x_5 and N respectively.

J_1, J_2, J_3, J_4 and J_5 are the probabilities of photo ionization of O_2, N_2, O, N, and NO. β_1, β_2 and β_3 are rate coefficients of the dissociative recombination reactions (21, *i*), (21, *ii*), and (21, *iii*) respectively.

If α_r ($r = 1, 2, 3 \ldots\ldots\ldots\ldots 9$) denotes the rate coefficients of ion atom interchange reactions (20), we obtain :

$$\dot{x}_1 = J_1 a + \alpha_2 . a . x_3 - x_1 (\alpha_5 d + \alpha_6 b + \beta_1 N) \quad (22)$$
$$\dot{x}_2 = J_2 b - x_2 . (\alpha_7 c + \alpha_8 d + \alpha_9 a + \beta_2 N) \quad (23)$$
$$\dot{x}_3 = J_3 c + \alpha_4 . a . x_4 - x_3 (\alpha_1 b + \alpha_2 a) \quad (24)$$
$$\dot{x}_4 = J_4 d + \alpha_8 . d . x_2 - x_4 (\alpha_3 + \alpha_4) . a \quad (25)$$
$$\dot{x}_5 = J_5 e + \alpha_1 . b . x_3 + \alpha_3 . a . x_4 + x_1 . (\alpha_5 d + \alpha_6 b) + x_2 . (\alpha_7 c + \alpha_9 a) - \beta_3 . N . x_5 \quad (26)$$

Using above equations, the ion distributions in the F-region are calculated after calculating the rate of photoionization of the atmospheric constituents and determining the rate coefficients α^s and β^s.

Rate of Photoionization :

The rate of production of photo-ions due to the photo-ionization of the *i*th constituent is calculated from the expression :

$$\sum_{\nu} n(h\nu)_z . n(i)_z . kvi = n(i)_z \sum_{\nu} n(h\nu)_z \, kvi = n(i)_z \, J_{iz}$$

where $n(h\nu)_z$—number of photons of frequency ν at an altitude of z km,
$n(i)_z$ - particle concentration of *i*th constituent at altitude z km,

kvi—absorption cross-section corresponding to frequency ν for the ith constituent

J_{iz}—probability of ionization of the ith constituent at an altitude of z km.

Tho number of photons, $n\,(h\nu)_z$ incident per cm^2 sec^{-1} corresponding to the frequency ν at an altitude z is given by,

$$n(h\nu)_z = n(h\nu)_\infty \exp\left(-\sum_i n(i)_z \, H_{iz} \, k_{\nu i}\right)$$

where, $n\,(h\nu)_\infty$ is the photon flux at the top of the atmosphere. Using the data of absorption coefficient given by Dalgarno and Perkinson (1960), Watanabe (1958), Aboud *et al* (1955) and Weissler *et al* (1952) and the values of $n(h\nu)_\infty$ taken from the results of rocket-borne experiments extrapolated by Hinteregger (1961), the rate of production of ions is calculated after obtaining the distribution of neutral particle from Miller (1957) and the scale heights H_{iz} from the ARDC model atmosphere of 1959. The calculated rate of production of different ions in the ionosphere at different altitudes is given in Table XIII.

TABLE XIII

Rate of production of ions by solar ultraviolet radiation in the wavelength region 1000 - 100 A

Altitude (km)	Rate of production cm^{-3} sec^{-1}			
	O_2^+	N_2^+	O^+	N^+
120	$1{\cdot}28\times10^{2}$	$1{\cdot}06\times10^{2}$	$1{\cdot}66\times10^{1}$	$1{\cdot}95\times10^{-1}$
140	$1{\cdot}78\times10^{2}$	$5{\cdot}60\times10^{3}$	$1{\cdot}05\times10^{3}$	$6{\cdot}02\times10^{1}$
150	$1{\cdot}40\times10^{2}$	$5{\cdot}94\times10^{3}$	$1{\cdot}06\times10^{3}$	$9{\cdot}15\times10^{1}$
160	$6{\cdot}34\times10^{1}$	$4{\cdot}21\times10^{3}$	$6{\cdot}44\times10^{2}$	$8{\cdot}73\times10^{1}$
180	$2{\cdot}86\times10^{1}$	$2{\cdot}09\times10^{3}$	$3{\cdot}52\times10^{2}$	$5{\cdot}94\times10^{1}$
200	$1{\cdot}08\times10^{1}$	$8{\cdot}99\times10^{2}$	$2{\cdot}16\times10^{2}$	$3{\cdot}88\times10^{1}$
220	4·20	$3{\cdot}95\times10^{2}$	$1{\cdot}32\times10^{2}$	$2{\cdot}48\times10^{1}$
240	1·77	$1{\cdot}83\times10^{2}$	$8{\cdot}21\times10^{1}$	$1{\cdot}6\times10^{1}$
250	1·18	$1{\cdot}28\times10^{2}$	$6{\cdot}58\times10^{1}$	$1{\cdot}32\times10^{1}$
260	$8{\cdot}01\times10^{-1}$	$9{\cdot}09\times10^{1}$	$5{\cdot}27\times10^{1}$	$1{\cdot}09\times10^{1}$
280	$3{\cdot}87\times10^{-1}$	$4{\cdot}74\times10^{1}$	$3{\cdot}52\times10^{1}$	7·54
300	$1{\cdot}98\times10^{-1}$	$2{\cdot}61\times10^{1}$	$2{\cdot}43\times10^{1}$	5·36
320	$1{\cdot}06\times10^{-1}$	$1{\cdot}51\times10^{1}$	$1{\cdot}72\times10^{1}$	3·94
340	$5{\cdot}95\times10^{-2}$	9·00	$1{\cdot}24\times10^{1}$	2·94
360	$3{\cdot}46\times10^{-2}$	5·54	9·13	2·24
380	$2{\cdot}07\times10^{-2}$	3·51	6·86	1·72
400	$1{\cdot}29\times10^{-2}$	2·30	5·26	1·35

The rate of production of ions by X-rays as calculated by Ghosh and Sharda Nand (1960, 1962) is given in Table XIV.

TABLE XIV

Rate of production of ions by solar x-rays

Altitude (km)	Rate of production of ions (cm^{-3} sec^{-1})			
	O^+	N_2	O^+	N^+
120	$1{\cdot}62\times10^2$	$5{\cdot}53\times10^2$	$8{\cdot}45\times10^2$	2·38
140	$4{\cdot}12\times10^1$	$1{\cdot}68\times10^2$	$2{\cdot}45\times10^2$	2·95
150	$1{\cdot}49\times10^1$	$7{\cdot}70\times10^1$	$1{\cdot}12\times10^2$	1·90
160	6·09	$3{\cdot}77\times10^1$	$5{\cdot}53\times10^1$	1·34

Determination of α^s *and* β^s :

Taking the observed distribution of electron density (Nisbet, 1960) and the rate of ion production given in above Tables, the values of α^s and β^s are fixed from Eqns. (22-26) to give the observed percentage composition of ions (Johnson, 1961), at 150 km. Using these values of α^s and β^s and Eqns. (22-26), the photo-equilibrium time (which is the time require to attain 1/eth concentration of the photoequilibrium concentration of the ions) for each ion is calculated and is given in Table XV.

TABLE XV

Time of photo-equilibrium for various ions

Altitude (km)	Time of photo-equilibrium for				
	O_2^+	N_2^+	O^+	N^+	NO^+
120	22·4 sec	0·22 sec	0·65 sec	11·96 sec	0·65 sec
160	1·03 mts	0·36 sec	28·3 sec	1·55 sec	28·8 sec
200	2·81 mts	1·02 sec	5·40 mts	9·35 sec	5·40 mts
240	1·88 mts	1·61 sec	35·0 mts	1·03 mts	35·0 mts
280	1·15 mts	1·43 sec	2·65 hrs	4·80 mts	2·65 hrs
320	1·16 mts	1·57 sec	9·53 hrs	17·67 mts	9·53 hrs
360	1·61 mts	2 25 sec	28·61 hrs	54·33 mts	28·61 hrs
400	2·21 mts	3·12 sec	75·56 hrs	2 44 hrs	75·56 hrs

It is seen from the above Table that (except for O^+ and NO^+ above 320 km) equilibrium is established within a short time. Taking above values of α^s and β^s and assuming photo-equilibrium, the ion distribution is calculated upto 300 km,

The comparison of the calculated ion distribution with that obtained by Johnson (1961), shows,

(*i*) that the calculated distributions do not agree with the observed one below and above 150 km and the disagreement is larger above 180 km, and

(*ii*) that the total number of positive ions is not equal to electron density.

It may be concluded, from the above, that the rate coefficients of the processes should vary with altitude. It is generally agreed that the dissociative recombination coefficient β^s are constant. Therefore, keeping β^s constant, α^s are fixed at each altitude to reproduce the observed (Johnson, 1961) ion distribution. It should be noted that effective recombination coefficient α_{eff} can be calculated from,

$$\alpha_{ff} = \frac{\beta_1 n(O_2^+) + \beta_2 \cdot n(N_2^+) + \beta_3 \cdot n(NO^+)}{N}$$

which agrees with those obtained by Havens *et al* (1954) (Table XVI).

TABLE XVI

Altitude variation of the effective recombination coefficient α_{eff}
(assuming $\beta_1 = 1 \times 10^{-8}$ cm^3/sec, $\beta_2 = 4 \times 10^{-7}$ cm^3/sec and β_3 as follows)

Altitude (km)	β_3 (cm^3 sec^{-1})	α_{eff} (cm^3 sec^{-1}) Calculated	Havens *et al* (1954)
120	$5{\cdot}5 \times 10^{-8}$	$5{\cdot}0 \times 10^{-8}$	$1{\cdot}6 \times 10^{-8}$
140	$1{\cdot}5 \times 10^{-7}$	$1{\cdot}4 \times 10^{-7}$	...
150	$1{\cdot}3 \times 10^{-7}$	$1{\cdot}1 \times 10^{-7}$	$1{\cdot}6 \times 10^{-8}$
200	$7{\cdot}5 \times 10^{-9}$	$4{\cdot}4 \times 10^{-9}$	$2{\cdot}0 \times 10^{-9}$
250	$3{\cdot}0 \times 10^{-9}$	$1{\cdot}1 \times 10^{-10}$	$1{\cdot}3 \times 10^{-10}$
300	$3{\cdot}0 \times 10^{-9}$	$1{\cdot}1 \times 10^{-11}$	$1{\cdot}6 \times 10^{-11}$
340	,,	$7{\cdot}2 \times 10^{-12}$	$5{\cdot}0 \times 10^{-12}$
360	,,	$7{\cdot}5 \times 10^{-12}$	$3{\cdot}0 \times 10^{-12}$
400	,,	$7{\cdot}41 \times 10^{-12}$	$1{\cdot}8 \times 10^{-12}$

The rate coefficient β_3 for the dissociative recombination of NO^+ with electrons could not be kept constant for all altitudes as assumed earlier. From Eqns. (22-26), it is seen that β_3 appears in the last equation and therefore is fixed in the end. If a fixed value of β_3 (say fixed at 150 km to be $1{\cdot}3 \times 10^{-7}$—cm.^{3}/sec) is kept, the density of NO^+ at lower altitude exceeds the electron dinsity which is not tenable. β_3 has to be taken as high as $1{\cdot}5 \times 10^{-7}$ cm^3/sec at 140 km which is decreased to $2{\cdot}3 \times 10^{-8}$ cm^3/sec at 180 km in order to reproduce the observed distribution of NO^+.

Rate Coefficients of Ion-atom Interchange Reaction:

The rate coefficients of ion-atom interchange reactions except for α_2 are not experimentally determined. α_2 has been measured by Dickinson and Sayers (1960) to be $2{\cdot}5 \pm 0{\cdot}4 \times 10^{-11}$ cm^3/sec at 300°K. Since the ion-atom interchange is a two body process, it's coefficient is likely to increase with temperature analogous to the rate coefficient of two-body chemical process. Bates and Nicolet (1960), pointed that the rate coefficients of these reactions should be an increasing function of temperature and that these might possess some activation energy or steric hinderance. We have, therefore assumed that the rate coefficients vary as,

$$\alpha_r = C_r . \exp(-E_r/R.T)$$

where, $r = 1, 2, 3, \ldots\ldots 9$, R is the gas constant and E_r represents the activation energy. Graphs between $\log_e \alpha_r$ and $1/T$ (the values of α^s are already fixed between 120 – 180 km) are plotted, which are found to be a straight line (Fig. 9). These

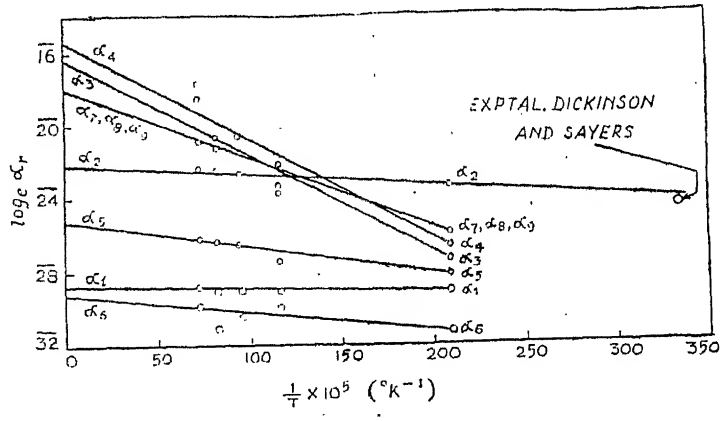

Fig. 9. Variation of rate-coefficients of ion atom interchange processes with the reciprocal of absolute temperature 1/T.

straight lines are then extrapolated to obtain α^s at higher altitudes (Table XVII) From Fig. 9, it is seen that the magnitudes of α^s do not differ appreciably above 200 km as 1/T remains approximately unchanged (ARDC model atmosphere 1959).

From table XVII, it is seen that the rate coefficients α_3 and α_4 of ion atom interchange reaction involving N^+ ion and O_2 molecule vary from 10^{-12} to 10^{-9} cm^3/sec and that their activation energies are very high, i. e. 7·74 Kcal. Since the density of N^+ ions is very small, the effect of these rate coefficients on the distribution of ions is small. The values of α_3 and α_4 above 180 km agree with the theoretically estimated order 10^{-9}/sec for such a reaction (Bates and Nicolet 1960). However, such a high value of rate coefficients has not been obtained for other reactions which usually vary between 10^{-13} to 10^{-10} cm^3/sec. Table XVII, further shows that reactions involving the same ion have nearly equal activation energies.

TABLE XVII

Temperature variation of rate coefficients of ion-atom interchange reactions. Quantities in paranthesis represent activation energies of reactions in kcal.

Altitude (km)	Temperature (°K)	Rate coefficient (cm^3/sec) α_1	α_2	α_3	α_4	α_5	α_6	$\alpha_7, \alpha_8, \alpha_9$
		(0·47)	(0·95)	(7·74)	(7·73)	(1·59)	(1·61)	(3·56)
120	477·0	$2{\cdot}0\times10^{-13}$	$7{\cdot}0\times10^{-11}$	$1{\cdot}3\times10^{-12}$	$2{\cdot}8\times10^{-12}$	$1{\cdot}0\times10^{-13}$	$9{\cdot}0\times10^{-14}$	$1{\cdot}5\times10^{-11}$
140	849·9	$2{\cdot}3\times10^{-13}$	$1{\cdot}2\times10^{-10}$	$1{\cdot}6\times10^{-10}$	$3{\cdot}3\times10^{-10}$	$5{\cdot}0\times10^{-12}$	$7{\cdot}0\times10^{-13}$	$2{\cdot}0\times10^{-10}$
150	1031·0	$2{\cdot}4\times10^{-13}$	$1{\cdot}3\times10^{-10}$	$5{\cdot}1\times10^{-10}$	$1{\cdot}0\times10^{-9}$	$6{\cdot}0\times10^{-12}$	$9{\cdot}0\times10^{-13}$	$4{\cdot}0\times10^{-10}$
160	1207·0	$2{\cdot}5\times10^{-13}$	$1{\cdot}5\times10^{-10}$	$1{\cdot}0\times10^{-9}$	$2{\cdot}0\times10^{-9}$	$6{\cdot}5\times10^{-12}$	$9{\cdot}5\times10^{-13}$	$5{\cdot}5\times10^{-10}$
180	1371·0	$3{\cdot}0\times10^{-13}$	$1{\cdot}6\times10^{-10}$	$1{\cdot}8\times10^{-9}$	$3{\cdot}8\times10^{-9}$	$7{\cdot}0\times10^{-12}$	$1{\cdot}0\times10^{-12}$	$7{\cdot}5\times10^{-10}$
200	1404·0	$3{\cdot}0\times10^{-13}$	$1{\cdot}6\times10^{-10}$	$1{\cdot}8\times10^{-9}$	$3{\cdot}8\times10^{-9}$	$7{\cdot}0\times10^{-12}$	$1{\cdot}0\times10^{-12}$	$7{\cdot}5\times10^{-10}$

The value of α_2 is found to be $3{\cdot}07 \times 10^{-11}$ cm^3/sec at 300°K which agrees with the experimentally determined value ($2{\cdot}5 \pm 0{\cdot}4 \times 10^{-11}$ cm^3/sec) of Dickinson and Sayers (1960) at the same temperature. We obtain the values of α_1 and α_2 for 1415°K to be 3×10^{-13} cm^3/sec and $1{\cdot}6 \times 10^{-10}$ cm^2/sec respectively. Bates and Nicolet (1960) also found that α_1 and α_2 differ by two orders at 250 km which according to ARDC model atmosphere 1959 has a temperature of 1415°K. It should however, be noted that the reactions (20, *vi*) and (20, *viii*) possess very small activation energies and therefore, they seem to be important reactions in the ionosphere. Reaction (20, *i*) is probably very important in the F_2-region where O^+ and N_2 molecules are in abundance. Through this reaction O^+ ions are converted into NO^+ ions which readily dissociate ($\beta_3 - 1 \times 10^{-8}$ cm^3/sec) into nitrogen and oxygen atoms. The dissociated atoms may exist in an excited states.

Effects of Diffusion and Vertical Drift of Ion Distribution.

Using the above values of α^s and β^s, ion densities are calculated, which are found to be lower than the observed values above 180 km. The discrepancy can be accounted for if diffusion is taken in the same proportion as the percentage of ions. (The magnitude of the diffusion contribution to the ionization can be estimated from the

difference between the calculated and the observed electron density variation with altitude). However, to obtain closer agreement, the vertical drift should also be considered.

From the expression of vertical drift, we have;

$$W = \frac{\partial (Nw}{\partial z}$$

and if it is assumed that drift velocity w, is constant with altitude then,

$$W = w \frac{\partial N}{\partial z}$$

After assuming that the difference in the total number of positive ions and electron density at 200 km is caused by the vertical drift, w is found to be about 16 meter/sec, This is of the same order as that obtained by Ferraro (1961), which according to him is about 10 meter/sec. The distribution of positive ions in the F-region of the ionosphere is given in Fig. 10.

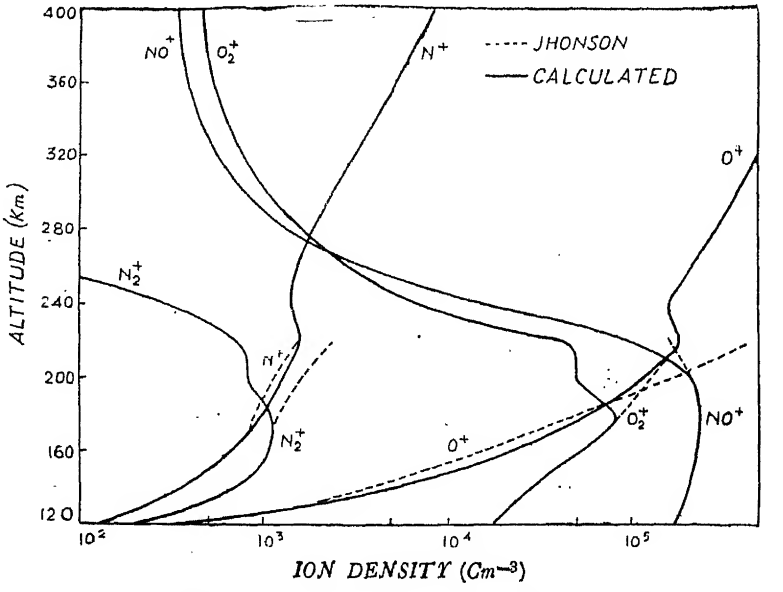

Fig 10. Distribution of positive ions in F - region of the ionosphere.

8. PHOTOCHEMICAL MODIFICATION OF MAJOR CONSTITUENTS OF MARTIAN ATMOSPHERE

The investigations of the Martian atmosphere which have been carried out uptil now, reveal that N_2, CO_2, A and some amount of O_2 and H_2O vapour are present in its atmosphere. From the absorption spectra of Martian atmosphere, Kuiper (1952) showed that CO_2 is present in its atmosphere, and he estimated its abundance to be 5·98 gm cm^{-2}. The composition of the remain-

ing constituents is obtained indirectly by Urey (1959) from the theories of origin of planetary atmospheres. He showed that the main constituents of the Martian atmosphere besides CO_2, are N_2 and some radiogenic argon. The amount of nitrogen is assumed to be 219 gm cm^{-2} in order to agree with the total scattering power and the total mass of the Martian atmosphere. These latter quantities were determined by Dollfus (1951) from the relative amounts of light scattered from the surface and that from its atmosphere. The total mass is estimated to be 227 gm cm^{-2}. The estimated values (Urey, 1959) of water vapour (0·042 gm cm^{-2}) and O_2 (0·35 gm cm^{-2}) are the upper limits obtained from the failure of detecting their presence in the absorption spectra of the atmosphere of Mars. The amount of argon is obtained after subtracting the amounts of N_2, O_2, CO_2 and H_2O from the total mass of the Martian atmosphere and is estimated to be about 1·28 gm^{-2}, which can be produced from the radioactive decay of K^{40} present in Mars. The table below gives the composition and certain characteristics of the Martian atmosphere at its surface.

TABLE XVIII

N_2	219·00 gm cm^{-2}
CO_2	5·98 gm·cm^{-2}
A	1·28 gm cm^{-2}
O_2	0·35 gm cm^{-2}
H_2O	0·04 gm cm^{-2}
Total mass of the atmosphere	227·00 gm cm^{-2}
Average surface temperature	300°K
Average Atmospheric pressure at the surface	$8·87 \times 10^4$ dynes cm^{-2}
g at the surface	391 cm sec^{-2}

Goody (1957) has estimated the variation of temperature with altitude in the Martian atmosphere, and is given by,

$$T_z = T_0 + \alpha(z - z_0)$$

where, T_z and T_0 are respectively the absolute temperatures at the altitude z and at the datum level of a region into which the Martian atmosphere has been divided. α is the temperature gradient. The table below shows the magnitude of the above quantities for the Martian atmosphere.

TABLE XIX

Region (km)	Datum altitude z_0 (km)	Temperature at the datum altitude T_0 (°K)	Temperature gradient α (°K km^{-1})
0 – 30	0	300·0	– 3·75
30 – 90	30	186·5	– 0·96
Above 90	90	130·0	+ 1·005

.... Assuming complete mixing of the constituents of the Martian atmosphere upto 130 km and neglecting the variation of g with altitude Ghosh and Sharma (1963) have calculated the altitude distribution of the constituent of the Martian atmosphere. Above 130 km the distribution is calculated after assuming the diffusive separation of the constituents (Fig. 11).

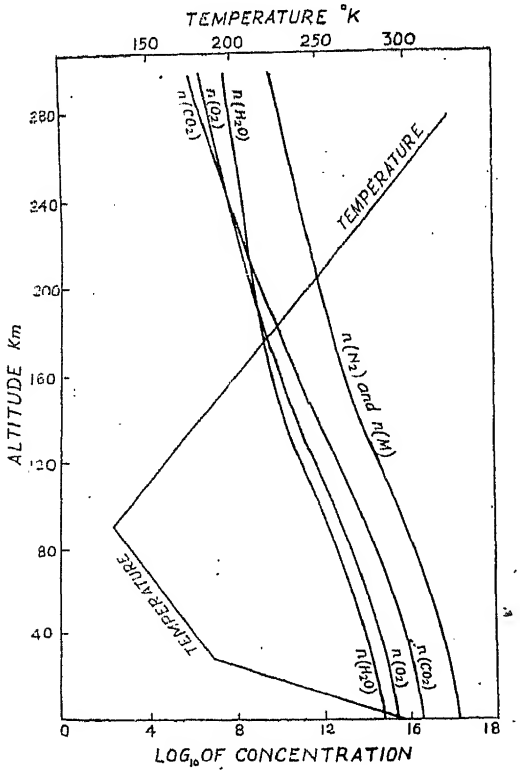

Fig. 11. Altitude distribution of temperature and main stable constituents of Martian atmosphere.

We shall now consider the distribution of the two main constituents (N_2 and CO_2) of the Martian atmosphere as modified by photochemical reactions. Due to solar ultraviolet radiations, N_2 is dissociated into two N atoms and CO_2 into CO and O. As these dissociated products are very reactive, they produce many chemical reactions leading to a complex photochemistry of the Martian atmosphere. We shall separately consider the photochemical modifications of N_2 and CO_2.

Altitude distribution of N_2 and N :

The N_2 molecules are photo-dissociated by the following predisscciation process

$$N_2 + h\nu \ (1076 \text{ A} < \lambda < 1267 \text{ A}) \rightarrow N + N$$

In addition to the above process, N atoms can be produced by the dissociative recombination with electrons of N_2^+ ions (produced by the ionization of N_2 molecules bv solar radiations below 1000 A.) Thus,

$$N_2^+ + e \rightarrow N + N$$

The relative importance of these two processes for the dissociation of N_2 molecules at different altitudes in the Martian atmosphere can be roughly estimated as follows. Assuming that in the upper atmosphere of Mars, solar radiations between 1267A and 1076A are mainly absorbed by N_2 molecules, the probability of predissociation of a N_2 molecule at an altitude z is given by (vide section 1),

$$n_1 . k_1 . \exp [-N(N_2)_z . k_1]$$

At the equilibrium condition, the rate of ionization of N_2 molecules by solar radiations below 1000 A is equal to the rate of dissociative recombination of N_2^+ ions with electrons. Considering that all the constituents of the upper atmosphere of Mars (N_2, CO_2, CO, N and O) strongly absorb radiations in this region, we obtain the probability of dissociative recombination of an N_2^+ ion with electrons,

$$n_2 . k_2 . \exp [- N (M)_z . k_2]$$

where, n_1 and n_2 – photon flux in the regions between 1267 A and 1076 A and below 1000 A respectively at the top of the Martian atmosphere.

k_1 and k_2—average absorption cross-section of the atmospheric constituents of Mars in the region 1267 A – 1076 A aod below 1000 A respectively

$N(N_2)_z$—number of N_2 molecules per cm^2 column above altitude z

$N(M)_z$—total number of molecules per cm^2 column above altitude z.

Therefore at the altitudes where predissociation predominates,

$$\exp [N (M)_z . k_2 - N (N_2)_z . k_1] > (n_2 . k_2) / (n_1 . k_1)$$

Substituting the values, one finds that below 270 km predissociation predominates over the dissociative recombination which may be neglected. The distribution of N and N_2 shall now be considered below 270 km.

Considering the recombination of N atoms by the three body process below 270 km (two-body radiative association of N atoms is a very slow process), we have at the equilibrium,

$$J_{N_2} . n(N_2) = \alpha . n(N)^2 . n(M) \qquad (27a)$$

where, $n(N_2)$, $n(N)$, and $n(M)$ are the equilibrium concentrations of N_2, N and the third body respectively. J_{N_2} and α are the probability of predissociation of N_2 molecules and the rate co-efficient of the three-body recombination process respectively. Assuming,

$$n_0 (N_2) = n (N_2) + 1/2 . n (N) \qquad (27b)$$

and solving Eqns. (27*a*) and (27*b*), we have

$$n (N) = \frac{J_{N_2}}{4 . \alpha . n (M)} \left[\left\{ 1 + \frac{16 . \alpha . n (M) . n_0 (N_2)}{J_{N_2}} \right\}^{1/2} - 1 \right] \qquad (28)$$

where, $n_0 (N_2)$ is the concentration of N_2 molecules obtained from the hydrostatic equilibrium of the Martian atmosphere and obtained earlier $n(N_2)$ is obtained from Eqn. (27*b*) after determining $n(N)$ from Eqn. (28). The distribution of N and N as modified by photochemical reaction is plotted in Fig. 12.

Altitude distribution of CO *and* CO_2

Carbon dioxide is disscciated by the absorption of radiation in the wavelength region 1750A—1050A (Section 1) by the process,

$$CO_2 + h\nu\ (1050\ A < \lambda < 1750\ A) \rightarrow CO + O$$

and assuming the recombination of CO and O by the following three-body process,

$$CO + O + M \rightarrow CO_2 + M \tag{29}$$

we have at the equilibrium condition,

$$J_{CO_2}.\ n\ (CO_2) = \beta.\ n\ (CO).\ n(O).\ n(M) \tag{30}$$

where, $n\ (CO_2)$, $n(CO)$ and $n(O)$ are the equilibrium concentrations of CO_2, CO and O respectively. J_{CO_2} and β are the probabilities of dissociation of CO_2 and the rate coefficient of the reaction (29). Assuming,

$$n_o(CO_2) = n(CO_2) + n(CO) \tag{31a}$$

and

$$n(CO) = n(O) \tag{31b}$$

where, $n_o(CO_2)$ is the concentration of CO_2 molecules obtained from the hydrostatic equilibrium of the martian atmosphere as obtained earlier. Solving Eqns. (30) and (31), we obtain

$$n(CO) = \frac{J_{CO_2}}{2.\ \beta n\ (M)}\left[\left\{\ 1 + \frac{4\beta.\ n(M).\ n_o\ (CO_2)}{J_{CO_2}}\right\}^{1/2} - 1\ \right]$$

The calculated distribution of CO_2 and CO as modified by photochemical reactions are plotted in Fig. 12.

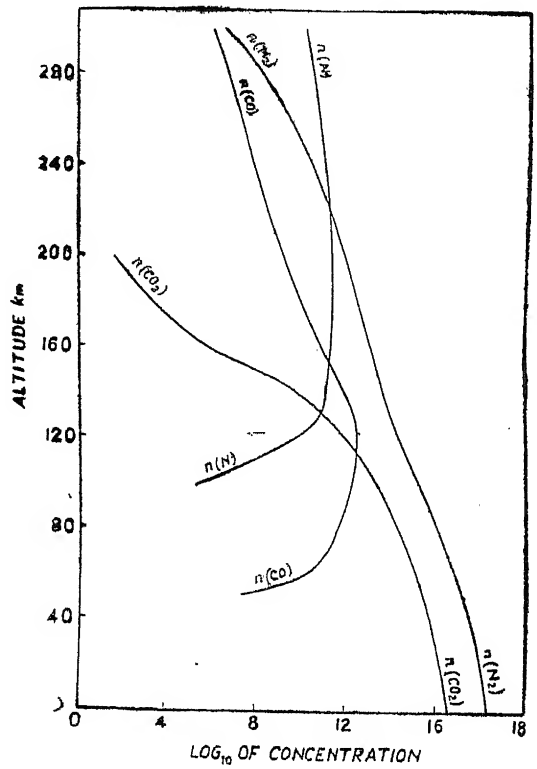

Fig. 12. Altitude distributions of N_2, N, CO_2 and CO in Martian atmosphere as modified by photodissociation of N_2 and CO_2.

In the above calculations the values of the rate coefficients α and β are taken to be $1{\cdot}72 \times 10^{-32}$ cm^6 sec^{-1} (Harteck *et al.* 1953) and 5×10^{-36} cm^6 sec^{-1} (Harteck and Dondes, 1955) respectively. The probabilities of dissociation J_{N_2} and J_{CO_2} are calculated as given in section 1.

The distribution of the dissociated products may be further modified by chemical reactions between N_2, CO_2 CO, and N. It is apparent from Figs. 11 and 1 , that the effect of the dissociation of O_2 (which is neglected in the present calculation) on the distributions of CO_2 and CO and O is negligible below 200 km owing to the low concentration of O_2, but becomes appreciable above this altitude. Although the concentrations of O^H and H (Produced by the photodissociation of H_2O by solar ultraviolet radiation below 1800 A, (see Watanabe *et al* 1953) may be very small below 200 km, but because of their reactivity the photochemistry of the Martian atmosphere can be altered considerably. Furthermore the reaction between N, N_2, O and O_2 can produce the oxides of nitrogen, which are recently suspected to be present in the Martian atmosphere (Kiess *et al* 1960).

It is to be noted from Fig. 11 that above 30 km, the atmosphere of Mars is denser than the terrestrial atmosphere (Vaucouleurs has also obtained the same result, 1950. The concentrations of dissociated species (CO, O, N OH and H) are also much higher. It is known from laboratory experiments that reactions between these constituents produce chemiluminescence and hence an airglow in the Martian atmosphere can be produced. The spectrum of the airglow is expected to contain CO_2 and CN band systems for the following reasons :

It is a well known fact that CO_2 bands are emitted from $CO-O_2$ flames at ordinary temperatures. According to Gaydon (1957), such band emission may be caused by the following reaction :

$$O + CO + M \rightarrow CO_2^* + M$$
$$CO_2^* \rightarrow CO_2 + h\nu$$

In the Martian upper atmosphere where both O and CO are present, CO_2 band emission is therefore expected. Again, recently Broida and Heath (1957), observed a luminous reaction between CO and N emitting red and violet system of CN. These bands of CN may also be present in the Martian airglow.

9. CONTROLLED REACTION BETWEEN FREE ATOMS AND MOLECULES IN GAS PHASE.

Controlled reactions between neutral particles, which lead to luminous glow and in which one of the reactants is an atom, are important not only for obtaining basic information of such reactions but also for increasing our knowledge of planetary atmospheres. To understand the importance of such reactions for the study of earth's upper atmosphere, one needs only to recall that a large number of molecules in the upper atmosphere are dissociated by solar ultraviolet rays. Being created in a tenuous atmosphere, these dissociated atoms and free radials do not recombine readily and therefore possess rather long life. Some times they react with other atoms and molecules present in the upper atmosphere producing in certain cases, chemiluminescence. From the photometry of the chemiluminescence, one should be able to obtain information of the reacting species. For example, if a gas is sprayed from a rocket which reacting with atmospheric gases produces a glow, then the distribution of atmospheric constituents can be determined (Pressman *et al*, 1956, Bedinger *et al*, 1958, and Zelikoff *et al*, 1958). Ghosh and Sharma and Sharda Nand (1962) has studied a chemiluminescent reaction between N atoms and methylene chloride.

(*i*) *Experimental*:

Since the reaction between atoms and free radials with molecules are fast processes, the state of the reaction and the non-equilibrium distribution of molecules (when population of molecules in their various levels of excitation does not follow Maxwell-Boltzmann distribution) vary rapidly with time. Therefore, a particular state of the reaction is rather difficult to obtain in a static system. On the other hand, by suitable adjustment of the flow of the reacting species in a dynamic system, the desired state of the reaction can be made steady in a certain portion of the system. Therefore, a dynamical flow method is adopted for such investigation. The reaction system is made of Pyrex glass and is illustrated in Figure 13.

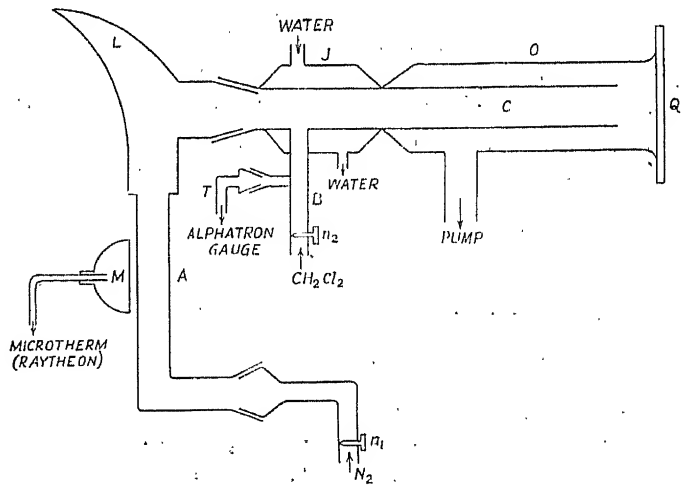

Fig. 13. Dynamical flow system for the study of glow produced by reaction between active nitrogen and methylene chloride.

The details have been described earlier (Ghosh, Sharma and Sharda Nand 1962).

In order to have clear understanding of the reaction mechanism, one needs the following information: (*i*) the reactants and the reaction products, (*ii*) the order of reaction (bimolecular, trimolecular etc.), (*iii*) the rate coefficient. The mechanism of a reaction can be established only when the reactants, final products and if possible, atoms molecules and free radicals produced in the intermediate reactions are definitely identified The study of the visible and ulter-violet spectrum of the reaction glow revealed information regarding the products of the reaction and is given in section *vi*). The mass-spectrometric analysis of the gas sample taken from the reaction chamber was carried out for the identification of the final products of the reaction and is given in section (*v*). In order to determine the order of the reaction producing the glow the variation of the intensity of the glow with the partial pressure of the reactants was obtained and is given in section (*iv*).

The rate coefficient of the reaction cannot be determined. It involves estimation of nitrogen atom concentration. Although methods have been devised for determining the concentration of oxygen or hydrogen atoms, no satisfactory method has yet been developed for determining nitrogen atom concentration.

(iii) *Spectroscopic Studies:*

As mentioned in the previous section; by mixing active nitrogen with CH_2Cl_2 vapour, a faint orange glow was obtained. A good spectrum was obtained with an exposure of 12 hours for O plates and 3 hours for F plates. On examining the spectrum it was found that between the spectral region 3000 Å and 7000 Å, CH bands (4312.5λ, 4315. Oλ) and the red and violet bands of CN are emitted (figure 14, Plate 1). Measured wavelengths of observed bands with their identifications are given by Ghosh, Sharma and Shardanand (1962).

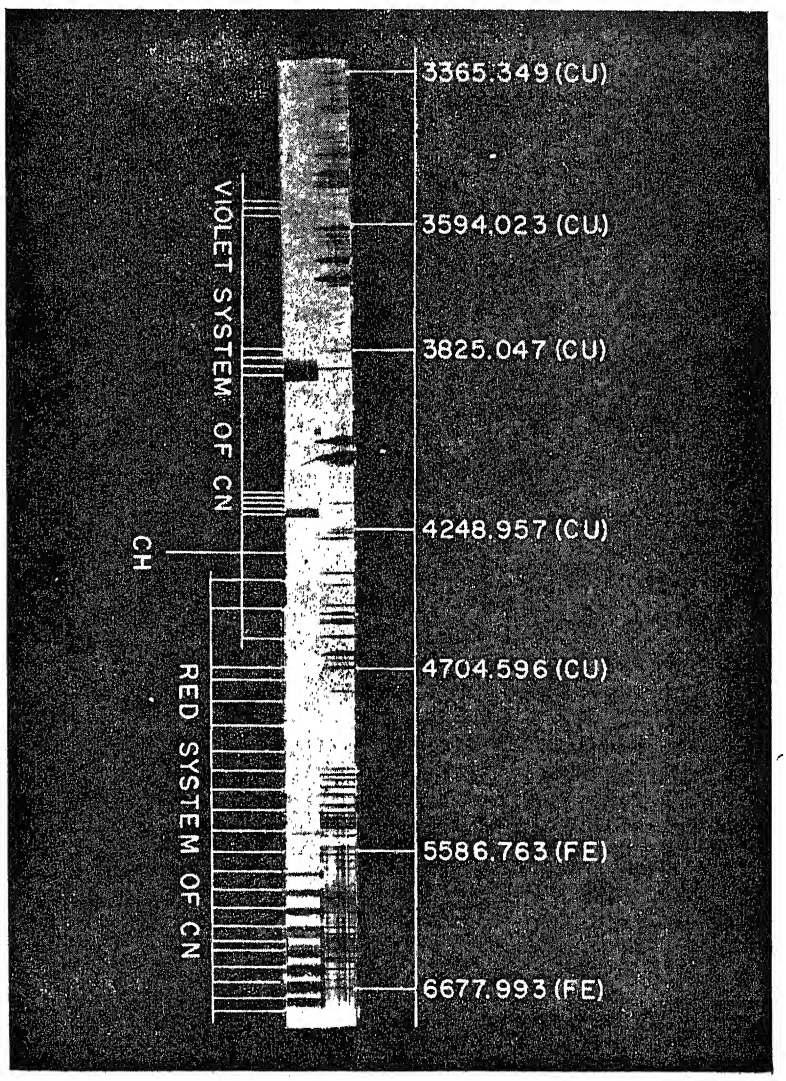

Fig. 14. Spectrum of glow produced by reaction between active nitrogen and methylene chloride in the region 2000 – 7000 A.

(iv) Photometric Study:

The CN violet system was a picked up with a Bausch and Lomb Monochromator of the type 33-86-40, using a grating of 250 mm focal length, 600 lines per mm and a dispersion of 66 Å mm^{-1}. The intensity was measured by a photomultiplier (RCA IP28) to which an ultrasensitive d. c. microammeter (RCA WV-848) was connected The voltages to the different dyanodes of the photomultiplier tube were applied from a superstable high voltage power supply (312A, Baird Atomic Inc.), which can give a maximum voltage of 1500 V. Keeping the flow of N_2 constant, the variation in the intensity of the glow with the partial pressure of CH_2Cl_2 vapour (recorded by an alphatron gauge, which was previously calibrated with respect to an oil manometer) was plotted (figures 15 and 16).

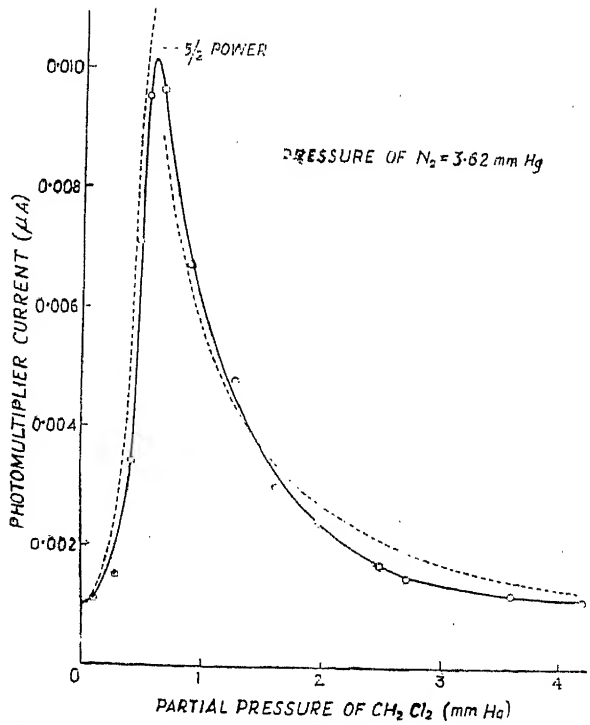

Fig. 15. Variation of intensity of the glow with the partial pressure of CH_2Cl_2, keeping a constant flow of N_2 (partial pressure of N_2 = 3·62 mm). Note that while the glow is being produced, the intensity varies as 5/2 power of pressure, whereas for quenching portion, the curve is a rectangular hyperbola.

It was found that with the increase of pressure of CH_2Cl_2 vapour, the intensity of the glow at first rose very rapidly and then attained a maximum, after which the glow was slowly quenched and finally at a total pressure of about 6 mm Hg the glow was completely quenched. The ultra-sensitive d. c. microammeter then read only the dark current of the photomultiplier tube. For higher flow of N_2 it was found that the nature of the curve is the same except that the maximum shifts to a lower pressure of CH_2Cl_2, and that the maximum intensity of the glow rises very quickly with pressure, a sufficient number of observations could not be taken. To compensate for this, several

curves relating the variation of intensity of the glow with the partial pressures of CH_2Cl_2 (for the same flow of nitrogen) were drawn and the mean of these curves was then plotted. Within the experimental error, it was found that while the glow is being produced the intensity varies as the 5/2 power of pressure, whereas for the quenching portion the curve is a rectangular hyperbola.

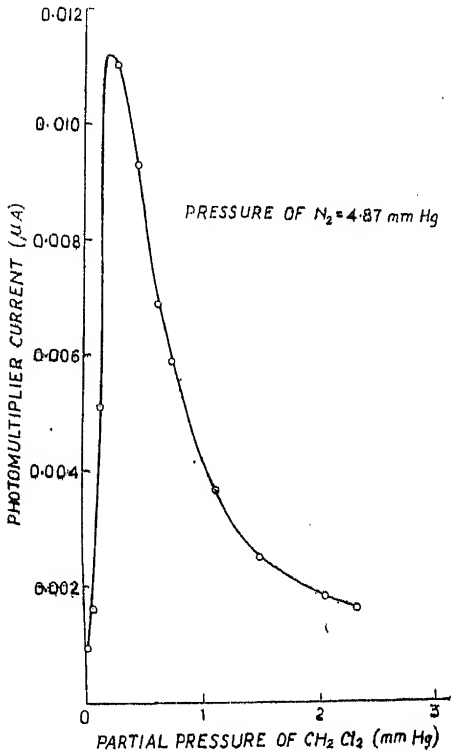

Fig. 16. Variation of intensity of the glow with the partial pressure of CH_2Cl_2, keeping a constant flow of N_2 (partial pressure of N_2 = 4·87 mm).

(*v*) *Mass Spectrometric Study*:

In order to determine the reaction products, the mass-spectroscopic analysis of the gas collected both during the discharge and when the discharge was off, was made by a beam type of mass spectromuter. The spectrum of the gas collected during discharge shows HCl line (Figure 17, Plate II).

(*vi*) *Quenching of Excited CN* Radicals by Methylene Chloride* :

The variation of the glow intensity with the partial pressures of CH_2Cl_2 molecules can be understood in the following manner. The excited CN* radicals which are mainly responsible for the glow, are produced as a result of the reaction between active nitrogen (normal and metastable N atoms, and metastable N_2 molecules) and CH_2Cl_2 molecules. As the partial pressure of methylene chloride is increased, the rate of formation of CN* increases up to a maximum

On further increasing the partial pressure, the rate of quenching of excited CN* radicals by CH_2Cl_2 molecules increases, thereby decreasing the intensity of the reaction glow.

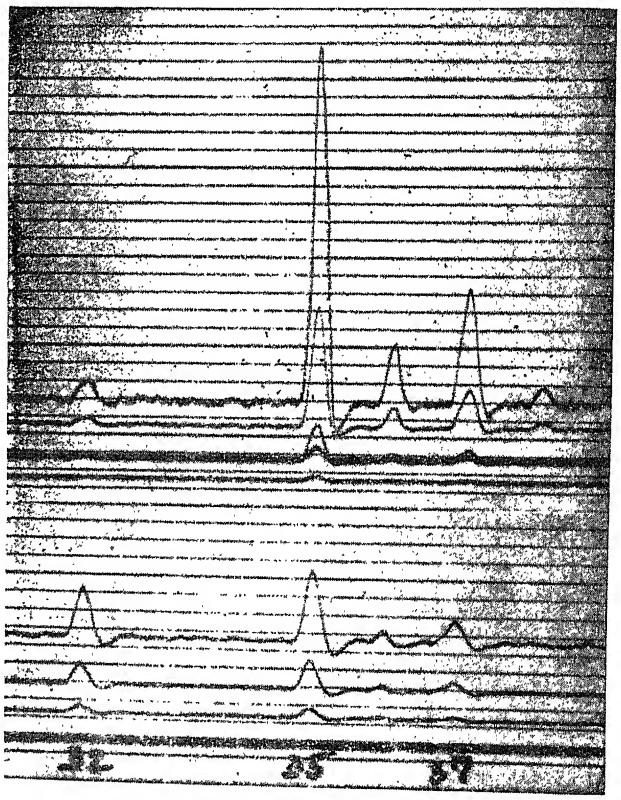

Fig. 17. Mass-spectrometric record of the gas collected (*a*) during discharge and (*b*) when discharge is off. Note that the spectrum of the gas collected during discharge shows the presence of HCl line.

Equating the rates of production and destruction of CN* radicals, we obtain

$$\beta . n\,(X)^a . n\,(CH_2Cl_2)^b = n\,(CN^*)\,[\,A + k_1 . n\,(\,(CH_2Cl_2)\,]$$

where β is the rate coefficient of the reaction, $n\,(X)$ the concentration of the species of the active nitrogen responsible for the glow, $n(CH_2Cl_2)$ the concentration of CH_2Cl_2 molecules, A the transition probability for the excited CN* radicals and k_1 the rate coefficient of the quenching process.

Therefore, the rate of emission of photons per cm^3 from the excited CN* radicals is given by

$$R = A . \frac{\beta . n\,(X)^a . n\,(\,(CH_2Cl_2)^b}{A + k_1 . n\,(CH_2Cl_2)}$$

The photomultiplier current which is proportional to R is given by

$$I = K.\ A.\ \frac{\beta.\ n\ (X^a).\ n\ (CH_2Cl_2)^b}{A + k_1.\ n\ (CH_2Cl_2)}$$

where the constant K depends upon the geometry of the reaction chamber and the sensitivity of the photometric system.

Assuming that rate of production of excited CN* radical becomes constant after attaining a maximum*, we have

$$\beta\ n\ (x)^a.\ n_M\ (CH_2Cl_2)^b = C$$

where $n_M\ (CH_2\ Cl_2)$ is the concentration of methylene chloride and C the rate of production of CN* radicals when the glow intensity is maximum.

Therefore, the maximum photomultiplier current is given by

$$_M = \frac{KCA}{A + k_1\ n_M\ (CH_2Cl_2)}$$

If at a higher concentration of $n'\ (CH_2Cl_2)$, the photomultiplier current is half that of the maximum, we have

$$\frac{A + k_1\ n'\ (CH_2Cl_2)}{A + k_1\ n_M\ (CH_2Cl_2)} \quad 2$$

or

$$K_1 = \frac{A}{|n'\ (CH_2\ Cl_2) - 2n_M\ (CH_2Cl_2)} \tag{33}$$

$n'\ (CH_2Cl_2)$ and $n_M\ (CH_2Cl_2)$ are obtained from the corresponding partial pressures of CH_2Cl_2 from figure 15. For this purpose, the temperature of the chamber is assumed to be 300°K. Also assuming $A = 10^8\ sec^{-1}$, one finds from equation (1), $k_1 = 10^{-8}\ cm^3\ sec^{-1}$. If k_1 is known, the quenching cross section σ^2 can be computed from the expression

$$\sigma^2 = k_1 \left[8\pi kT \left(\frac{1}{m_{CN}} + \frac{1}{m_{CH_2Cl_2}} \right) \right]^{-1/2}$$

where k is Boltzmann's constant, T the absolute temperature of the reaction chamber and m_{CN} and $m_{CH_2\ Cl_2}$ the molecular masses of CN and $CH_2\ Cl_2$ molecules respectively. Substituting in the above expression we obtain $\sigma^2 = 1{\cdot}8 \times 10^{-14}\ cm^2$. It may be mentioned that Carrington (1959) found the quenching cross section of the electronically excited OH radical by H_2O to be $3{\cdot}5 \times 10^{-15}\ cm^2$. Considering the reactivity of CN radicals with hydrocarbons, the above quenching cross section is justified.

*While studying the reaction between active nitrogen and hydrocarbons in a dynamic system, Winkler and Schiff (1953) reported that the rate of production of HCN at first increases directly with the flow of ethylene, then attains a maximum and afterwards remains contant,

(vii) Discussion:

From the spectroscopic analysis (section *iii*), we have found that the glow in the visible region is due to red and violet system of the CN radicals. Also the mass-spectroscopic analysis of the gas collected near the place where the glow is maintained shows the presence of HCl molecules. We may therefore assume the following reaction† for the production of excited CN* radicals:

$$N' + CH_2Cl_2 \rightarrow CN^* + 2HCl \qquad (34)$$

where N′ and CN* represent the nitrogen atom (normal or metastable) and the excited CN radical respectively. From energy considerations we have

$$D(CN) + 2D(HCl) + E(N') > H(CH_2Cl_2) + E(CN^*) \qquad (35)$$

where D (CN) and D(HCl) are the dissociation energies of the CN and HCl molecules respectively, H (CH_2Cl_2) is the sum of the energies of two C-H and two C—Cl bonds in CH_2Cl_2 and E (N′) and E (CN*) are the excitation energies of N′ atoms and CN* radicals respectively.

The bond energies for HCl, CN and CH_2Cl_2 are collected in table XX and the excitation energies of N′ and CN* are given in table XXI.

TABLE XX

Molecule	Bond	Bound energy (eV)	Reference
HCl	H-Cl	4·5	Herzberg (1950)
CN	C-N	4·5 – 7·6	Herzberg (1950)
CH_2Cl_2	C-H	4·02	Semenov (1958)
CH_2Cl_2	C-Cl	3·40	Semenov (1958)

TABLE XXI

Atom or radical	State	Excitation energy (ev)
N	^4S	0
	^2D	2·37
	^2P	3·56
CN	$X^2\Sigma^+$	0
	$A^2{}_i\pi$ ($v'=10$)	3·3
	$B^2\Sigma^+$ ($v'=5$)	4·5

It may be noted that the above reaction for the production of CN radicals can not explain the 5/2 power law of intensity variation with the partial pressure of CH_2Cl_2. The excited CN radicals are therefore produced by a more complicated reaction than the one assumed.

The highest vibrational levels v' involved in the observed bands of CN are given in table XXI.

From condition (35) we obtain

$$D(CN) > H(CH_2Cl_2) + E(CN^*) - 2D(HCl) - E(N') \qquad (36)$$

for $H(CH_2Cl_2)$, it is assumed that

$$H(CH_2Cl_2) = 2D(CH_2Cl_2 - Cl) + 2D(CHCl_2 - H)$$

where $D(CH_2Cl - Cl)$ and $D(CHCl_2 - H)$ are energies of C–Cl and C–H bonds in CH_2Cl_2 molecules. It may, however, be noted that the actual sum of the energies of two C – H and C – Cl bonds should be slightly less than that obtained from the above assumption.

In general, the required value of D(CN) depends on the electronic states of N' and CN* radicals. Using the data collected in tables XX and XXI, D(CN) can be computed from condition (36). For different combinations of electronic states of N' and CN*, the lower limit of D(CN) is given in table XXII.

TABLE XXII

Electronic state of N'	Electronic state of CN*	Lower limit of D(CN) (ev)
^4S	$X^2\Sigma^+$	5·8
	$A^2\pi_i$	9·1
	$B^2\Sigma^+$	10·3
^2D	$A^2\pi_i$	4·7
	$B^2\Sigma^+$	7·9
^2P	$A^2\pi_i$	3·5
	$B^2\Sigma^+$	6·7

Assuming the dissociation energy of CN to lie between the limits given in table XX, it can be concluded from table XXII that from energy considerations, a normal $N(^4S)$ atom can produce an unexcited CN $(X^2\Sigma^+)$ radical, a metastable $N(^2D)$ atom $CN(X^2\Sigma^+)$ and $CN(A^2\pi_i)$ and $N(^2P)$ atom can produce a CN radical in $X^2\Sigma^+$ $A^2\pi_i$ and $B^2\Sigma^+$ states. Since the relative abundance of normal and metastable nitrogen atoms in the active nitrogen is not known, it cannot be definitely concluded that the excited CN radical is directly produced by reaction (34). An alternative reaction for the production of excited CN radical is as follows :

$$CN(X^2\Sigma^+) + (N^* \text{ or } N_2^*) = CN(A^2\pi_i \text{ or } B^2\Sigma^+) + (N \text{ or } N_2) \qquad (37)$$

where, N* and N_2* are the metastable nitrogen atoms and molecules The unexcited $CN(X^2\Sigma^+)$ radical is produced by the reaction (34). Regarding the presence of metastable N_2 molecules, it may be recalled that the intense first positive system of N_2 is observed in the spectrum of the microwave dischare through N_2. After emitting this system the N_2 molecules arrive at the metastable $A^3\Sigma$ state.

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COLLISIONAL PROCESSES IN GEOPHYSICAL AND CHEMICAL PROBLEMS

ENERGY LOSS AND SCATTERING OF RADIATION BELT ELECTRONS IN THE EARTH'S MAGNETOSPHERE*

By

A. M. LENCHEK† *and* S. F. SINGER

Physics Department, University of Maryland, College Park, Maryland, U.S.A.

ABSTRACT

For *fast* electrons moving through a hydrogen plasma the ions and plasma electrons are equally effective in producing deflections (contrary to some intuitive estimates). We show in detail how to calculate the scattering and energy loss for the case of a real atmosphere containing neutral and ionized oxygen, and neutral and ionized hydrogen. Finally we briefly discuss the application of these results to the geomagnetically trapped electrons.

INTRODUCTION

The magnetosphere is that region surrounding the earth wherein the motion of charged particles is controlled by the earth's magnetic field. The electrons trapped in this region move through a partially ionized gas consisting of hydrogen and oxygen. Above about 1500 km the major constituent is hydrogen. Coulomb interactions have two effects. The energy of the trapped electron is dissipated and its pitch angle is altered. When a trapped electron loses most of its energy *or* its pitch angle becomes so small that it mirrors in the *dense* atmosphere (below $\sim$ 1200 km) the electron is effectively removed from the trapping zone.

In section 1 we discuss the Coulomb interactions, obtaining the mean square deflection rate and the rate of energy loss for a fast ($E >> kT$) electron moving through a plasma.

In section 2 we briefly outline the application of these effects to trapped particle dynamics.

1. SCATTERING AND ENERGY LOSS

We wish to examine the scattering and energy loss of a fast electron moving through a plasma of protons and electrons. While this is a well-known, often solved problem, some ambiguity still exists in the literature concerning the relative effectiveness of protons *vs* electrons in producing angular deflection of the incident particle. In a recent paper Kellogg (1960) states that the protons are four times more effective then the ambient electrons. In the deflection of *thermal* electrons in a fully ionized hydrogen plasma, protons are indeed four times more effective [Öpik, 1961]. However, we emphasize that this applies to the deflection of thermal electrons. We shall now consider the scattering of *fast* electrons ($E >> kT$) in some detail and show that protons and electrons are essentially *equally* effective in producing deflection.

The quantity of interest is the mean square deflection per second since the scattering is a random process and accumulates at a rate such that the mean

*Supported by Grant No. AF-AFOSR - 62-284 ; Technical Report No. 239.

†R. H. Goddard Memorial Fellow of the National Rocket Club, Washington, D. C.

squared deflection is proportional to the time. If we call $<\theta^2>$ the mean square deflection per second (*i.e.*, radians^2 sec^{-1}) and if $\sigma(\theta)$ is the differential cross section, defined such that the number of particles scattered into thes olid angle $2\pi\sin\theta\, d\theta$ sec^{-1} is related to the incident flux j by $2\pi j\sigma(\theta)\sin\theta d\theta$, then

$$<\theta^2> = 2\pi\rho\beta c \int_{\theta_1}^{\theta_2} \theta^2\sigma(\theta)\sin\theta\, d\theta \qquad (1\cdot1)$$

Here ρ is the number of scattering centers per cm^3, βc is the (lab) velocity of the fast electron. The limits of integration are the minimum and maximum possible scattering engles, which can be related to maximum and minimum possible impact parameters.

Since we observe the deflection relative to a coordinate frame fixed in the lab all quantities in (1·1) are to be evaluated in the lab frame. We begin therefore by computing $\sigma(\theta)$ in the *lab* frame. We shall do this by first computing the cross section in the center of mass system, where it takes on a simple form, and then transforming to the lab system.

For the case of electrons scattered by protons we can regard the proton as being infinitely massive compared to the electron. Then the *center-of-mass* system coincides with the lab system. The cross section is, of course, the Rutherford cross section:

$$\frac{d\sigma(\theta)}{d\omega} = \tfrac{1}{4}\left(\frac{ZZ'e^2}{p\beta c}\right)^2 \frac{1}{\sin^4(\theta/2)} \cong \tfrac{1}{4}\left(\frac{ZZ'e^2}{2E}\right)^2 \frac{1}{\sin^4(\theta/2)} \qquad (1.2)$$

The first expression is correct in general; we shall restrict ourselves to nonrelativistic velocities. E is the kinetic energy of motion relative to the fixed force center. If the force center is at rest in the lab then E is just the lab energy. Call the lab energy W.

To simplify the notation we will temporarily set

$$\frac{(ZZ'e^2)^2}{16} = 1$$

Then (1.2) may be written:

$$\frac{d\sigma(\theta)}{d\omega} = \frac{1}{W^2\sin^4(\theta/2)} \equiv \sigma_{ep} \qquad (1.3)$$

We have inserted E = W.

We turn now to the case of fast electrons scattered by electrons at rest. Since the target electron, unlike a target proton, recoils significantly during the scattering process it is tempting to assume that the scattering is reduced compared to the electron-proton case. The correct cross section is not obtained from the former case merely by replacing the incident particle's mass by the reduced mass. In fact, that procedure results in the energy being replaced by $W/2$ and the cross section being *increased* by a factor of four. Let us instead actually carry out the calculation of the cross section.

We begin by noting that in the center-of-mass system the two-body motion reduces to the motion of a single fictitious particle having the reduced mass and moving in the field of a fixed center of force with the velocity equal to the relative velocity. Since the target electron is initially stationary in the lab, the relative velocity when the two electrons are far apart is just the lab velocity, v, of the incident electron. The situation is just that covered by the Rutherford cross section; the *center-of-mass* cross section is therefore

$$\overline{\sigma_{ee}}(\chi) = \frac{1}{E^2 \sin^4(\chi/2)} \tag{1.4}$$

We shall denote CM cross sections by bars and CM scattering angle by χ. Note that

$$E = \tfrac{1}{2}\mu v^2 = \tfrac{1}{4} m v^2 = \tfrac{1}{2} W \tag{1.5}$$

since the reduced mass $\mu = m/2$.

We must now transform this CM cross section into the corresponding lab cross section. Assume that the incident electron is not relativistic. By simply adding velocity vectors we find, in general,

$$\tan\theta = \frac{\sin\chi}{\cos\chi + (m/M)} \tag{1.6}$$

where m is the incident particle's mass and M is the target particle's mass. Here $m = M$ and

$$\tan\theta = \frac{\sin\chi}{\cos\chi + 1} = \tan\frac{\chi}{2} \tag{1.7}$$

Hence

$$\theta = \frac{\chi}{2} \tag{1.8}$$

Insertion of this familiar relation into (1.4) does not complete the transformation. Since the number of particles scattered into a given solid angle in one coordinate system must equal the number scattered into the corresponding solid angle in the other system we require that

$$2\pi j\ \bar{\sigma}(\chi) \sin\chi\, d\chi = 2\pi j \sigma(\theta) \sin\theta\, d\theta \tag{1.9}$$

or

$$\sigma(\theta) = \bar{\sigma}(\chi) \frac{d\cos\chi}{d\cos\theta} \tag{1.10}$$

Differentiating (1.7) we find

$$\frac{d\cos\chi}{d\cos\theta} = 4\cos\theta \tag{1.11}$$

Therefore,

$$\sigma(\theta) = 4\cos\theta\,\overline{\sigma}(\chi) \tag{1.12}$$

Inserting (1.8)

$$\sigma(\theta) = 4\cos\theta\ \ \sigma(2\theta) \tag{1.13}$$

Now

$$\overline{\sigma}_{ee}(2\theta) = \frac{1}{E^2\sin^4\theta} \tag{1.14}$$

and therefore

$$\overline{\sigma}_{ee}(2\theta) = \frac{4}{W^2\sin^4\theta} \tag{1.15}$$

since $E = W/2$.

Thus

$$\sigma_{ee}(\theta) = \frac{16\cos\theta}{W^2\sin^4\theta} \tag{1.16}$$

Eqs. (1.3) and (1.16) give the desired *laboratory* cross sections in terms of lab energy and lab scattering angle. We should now carry out the integration in Eq. (1.1). However, we can recall that for Coulomb scattering the predominant contribution to the mean deflection is made by *small-angle*-scatterings. In that case we may set

$$\cos\theta \simeq 1$$
$$\sin\theta \simeq \theta \tag{1.17}$$

Then both Eq. (1.3) and (1.16) reduce to the same result

$$\sigma_{ep} = \sigma_{ee} = \frac{16}{W^2\theta^4} \tag{1.18}$$

demonstrating that protons and electrons are essentially equally effective in producing angular deflection of fast electrons.

We shall now evaluate the deflection rate explicitly :

$$\langle\theta^2\rangle = 2\pi\rho\,\beta C\int_{\theta_1}^{\theta_2}\theta^2\sigma_{ep}(\theta)\sin\theta d\theta = 2\pi\rho\,\beta c\left(\frac{ZZ'e^2}{4W}\right)^2\int_{\theta_1}^{\theta_2}\frac{\theta^2\sin\theta d\theta}{\sin^4(\theta/2)} \tag{1.19}$$

Assuming $\theta << 1$ always, where ρ is now electron density plus proton density,

$$\langle\theta^2\rangle = 32\pi\rho\,\beta c\left(\frac{ZZ'e^2}{4W}\right)^2\int_{\theta_1}^{\theta_2}\frac{d\theta}{\theta} = 2\pi\rho\ \beta c\left(\frac{e^2}{W}\right)^2 ln\,(\theta_2/\theta_1) \tag{1.20}$$

Recall that the more general form of the cross section is obtained by replacing $2W$ by $p\beta c = mc\beta^2(1-\beta^2)^{-\frac{1}{2}}$. With this substitution, and setting the incident particle's $Z' = 1$, we obtain

$$\langle\theta^2\rangle = \frac{8\pi\rho\, c\, Z^2 e^4 (1-\beta^2)}{m^2c^4\beta^3} \ln(\theta_2/\theta_1) \tag{1.21}$$

or

$$\langle\theta^2\rangle = 8\pi\rho\, r_0^2 c Z^2 \frac{(1-\beta^2)}{\beta^3} \ln(\theta_2/\theta_1) \tag{1.22}$$

where $r_0 = e^2/mc^2$.

The minimum scattering angle, θ_1 will be set by the maximum impact parameter, $b_{max} \simeq \lambda_D$, the Debye length. Here the impulse approximation is valid :

$$\theta_1 = \frac{p_t}{p} = \frac{F\Delta t}{p} = \frac{(Ze^2/b^2)(2b/\beta c)}{p} = \frac{2Ze^2}{\lambda_D p\beta c} \tag{1.23}$$

The maximum scattering angle, θ_2, will be set by the minimum impact parameter, b_{min}. Several factors may limit b_{min}. Firstly b_{min} cannot be smaller than the dimensions of the particles involved. At momenta very much greater than mc, the maximum scattering angle is (Rossi, 1952, p. 66.)

$$\theta_2 = 280\, A^{-1/3} \frac{mc}{p} \tag{1.24}$$

This restriction does not apply to radiation belt electrons since their energies are far too small.

Secondly, b_{min} should be limited by the uncertainty principle, *i. e.*,

$$b_{min} \gtrsim \frac{\hbar}{p} \tag{1.25}$$

If the Coulomb energy of the electron at a distance b_{min} from the scatterer is small compared to the electron's kinetic energy the deflection will be small, allowing the use of the impluse approximation. This requires

$$\frac{Ze^2/b_{min}}{E} = \frac{Ze^2}{\hbar c}\frac{pc}{E} = \frac{Z}{137}\frac{pc}{E} << 1 \tag{1.26}$$

For small Z and $E \gtrsim 5$ kev this condition is satisfied.

Thus both θ_1 and θ_2 are given by the impulse approximation, from which it follows that

$$\theta_2/\theta_1 = \lambda_D/b_{min} = \lambda_D p/\hbar \tag{1.27}$$

We have, therefore, from (1.23)

$$\langle\theta^2\rangle = 8\pi\rho\, r_0^2 c\, Z^2\, \frac{(1-\beta^2)}{\beta^3}\, ln\,(\lambda_D p/\hbar) \tag{1.28}$$

as the final result. For the electrons in the magnetosphere $ln\ (\lambda_D p/\hbar) \simeq 23$.

The factor $(1 - \beta^2)$ represents the increase of mass with velocity which reduces the deflection as $\beta \rightarrow 1$. This factor plays an important role in determing the relative importance of scattering and *energy-loss* in lifetime calculations. The energy-loss rate does not exhibit this continuing decrease as $\beta \rightarrow 1$.

Scattering from neutral or partially ionized atoms can be treated in just the same way, the only difference being in the choice of θ_1. The shielding distance is now the atomic radius, r_a, instead of λ_D. On the Fermi-Thomas model.

$$r_a = \frac{r_0}{\alpha^2 Z^{1/3}} \tag{1.29}$$

where $\alpha^{-1} = \hbar c/e^2 = 137$. Then

$$ln\ (\theta_2/\theta_1) = ln\ (r_a/b_{min}) = ln\left[\frac{137}{Z^{1/3}}\ \frac{pc}{mc^2}\right] \tag{1.30}$$

For hydrogen and $pc \sim mc^2$ this factor is $\sim ln\ 137 = 4.9$. This means that fully ionized hydrogen is about 5 times more effective for scattering than neutral hydrogen. The difference is due to the fact that in ionized gas $b_{max} = \lambda_D \sim 1$ cm while for neutral gas $b_{max} \sim r_a \sim 10^{-8}$ cm. In both cases $b_{min} \sim 10^{-10}$ cm. Thus we have, in hydrogen,

ionized : $ln\ (b_{max}/b_{min}) = ln\ (1/10^{-10}) = 23$

neutral : $ln\ (b_{max}/b_{min}) = ln\ 10^2 = 4{\cdot}6$

If the atmosphere consists of a mixture of neutral and ionized components, the scattering is the sum of individual contributions. Let ρ_i represent tbe density of the i^{th} component. Then

$$\langle\theta^2\rangle = 8\pi r_0^2 c\, \frac{(1-\beta^2)}{\beta^3} \sum_i \rho_i Z_i^2\, ln\Lambda_i \tag{1.31}$$

where $\Lambda_i = (\theta_2/\theta_1)$ appropriate to the nature of the component, *i. e.*, free or bound. Care must be exercised in the choice of Z_i. For a *fully* ionized gas Z_i for the nuclei is just the atomic number while Z_i for the electrons is always unity. However, in this case the electron density is Z times the density of nuclei. Therefore a fully ionized gas can be treated by setting $Z_i^2 = Z(Z + 1)$ and $\Lambda_i = \lambda_D p/\hbar$.

For a neutral gas we can again set $Z_i^2 = Z(Z + 1)$ but now Λ_i is given by (1.30).

A partially ionized gas can be regarded as a mixture of a neutral gas, a free-electron gas and an ion gas. The nucleus of a partly ionized atom appears as a charge Ze for impact parameters small compared to the atomic radius and appears as a charge Ne, where N is the number of electrons lost by the atom, for impact parameters between the atomic radius and the Debye shielding distance. The combination of these two effects is proportional to $Z^2 \ ln \ (r_a/b_{min}) + N \ ln \ (\lambda_D/r_a)$.

As typical values take $\lambda_D = 1$ cm, $r_a = 10^{-8}$ cm, $b_{min} = 10^{-10}$ cm. Then this factor is

$$4{\cdot}6 \ Z^2 + 18{\cdot}4 \ N.$$

Unless $Z >> 1$ these two terms will be comparable. Adding the contribution of the electrons, both bound and free, the effect of a partly ionized component is given by setting

$$\rho_i \ Z_i^2 \ ln \ \Lambda_i = \rho \ Z(Z+1) \ ln \left[\frac{137}{Z^{1/3}} \frac{pc}{mc^2}\right] \tag{1.32}$$

$$+ \rho^+ \left\{ (Z^2+Z-N) \ ln \left[\frac{137}{Z^{1/3}} \frac{pc}{mc^2}\right] \quad N \left[ln \ (\lambda_D/r_a) + ln \ (\lambda_D/b_{min})\right] \right\}$$

where ρ and ρ^+ are the densities of neutral and ionized components, respectively. Since $\rho + \rho^+ = \rho_i$ we can also write the right side as

$$[\rho_i \ Z \ (Z+1) - 2\rho^+ N] \ ln \ (r_a/b_{min}) + 2\rho^+ N \ ln \ (\lambda_D/b_{min}), \ N \neq Z.$$

For $N = Z$ we must replace $\rho_i Z_i^2 ln \Lambda_i$ by $\rho_i \ Z_i \ (Z_i + 1) \ ln \ (\lambda_D/b_{min})$.

For magnetosphere conditions, we can now define an *effective* density for scattering, ρ_S, which expresses the density of any component of the magnetosphere in terms of that density of free electrons which produces the equivalent scattering rate. We write

$$\rho_S \ ln \ (\lambda_D/b_{min}) = \sum_i \rho_i \ Z_i^2 \ ln \ \Lambda_i \tag{1.33}$$

and evaluate all log terms for typical magnetosphere density ($10 < N_e < 10^5$ cm^{-3}) and temperature ($10^2 - 10^5$ °K) and for 1 kev $\lesssim$ E < 5 Mev. Under these conditions $ln \ (\lambda_D/b_{min}) = 23$ to within $\sim 10\%$.

Then, for fully ionized hydrogen :

$$\rho_S \ (H^+) = 2\rho \ (H^+) \tag{1.34.1}$$

For neutral hydrogen :

$$\rho_S \ (H) = \frac{2}{5} \rho(H) \tag{1.34.2}$$

For singly ionized oxygen :

$$\rho_S(O^+) = 16{\cdot}2\,\rho(O^+) \tag{1.34.3}$$

For neutral oxygen :

$$\rho_S(O) = 14{\cdot}4\,\rho(O) \tag{1.34.4}$$

Thus, the *effectiveness* per atom *relative to fully ionized hydrogen* is 1/5 for neutral hydrogen, 8·1 for ionized oxygen and 7·2 for neutral oxygen. (Note that becouse of the Z^2 dependence of the scattering process, a gas of bare oxygen nuclei would be $\frac{64+8}{2} = 36$ times as effective as fully ionized hydrogen.) These results are summarized in Table 1,1.

TABLE 1·1

Multiply true density by following factors to obtain effective scattering densities ρ_s.

Material	Conversion Factor
Fully ionized hydrogen	2·0
Neutral hydrogen	0·4
Singly ionized oxygen	16·2
Neutral oxygen	14·4

The deflection rate now can be written

$$\langle\theta^1\rangle = 8\pi r_0^2 c\rho_S \frac{(1-\beta^2)}{\beta^2} \ln(\lambda_D p/\hbar) \tag{1.35}$$

$$= 1{\cdot}38 \times 10^{-12}\,\rho_S \frac{(1-\beta^2)}{\beta^3}\,(\text{radians})^2\text{sec}^{-1}$$

The rate of energy-loss of a fast electron may be calculated in a manner similar to the calculation of $\langle\theta^2\rangle$. The quantity of interest is the mean energy-loss per second. We assume small-angle scattering and the impulse approximation. The momentum p_t transferred to the target particle, mass M, is related to the scattering angle through Eq. (1.23) The energy carried away by the target particle is $\Delta E = p_t^2/2M$ It is immediately clear that electrons are much more efficient in absorbing energy than protons. Considering collisions only with electrons the mean energy-loss per second is

$$\langle\Delta E\rangle = \frac{dE}{dt} = -2\pi\rho Z\beta c \int_{\theta_1}^{\theta_2} \Delta E(\theta)\,\sigma(\theta)\sin\theta\,d\theta \tag{1.36}$$

Now $\Delta E(\theta) = \frac{p_t^2}{2m}$

and

$$p_t^2 = p^2\,\theta^2 = \frac{m^2 c^2 \beta^2}{(1-\beta^2)}\,\theta^2.$$

Therefore

$$\Delta E\,(\theta) = \tfrac{1}{2}\,\frac{mc^2\,\beta^2}{(1-\beta^2)}\,\theta^2$$

and

$$<\Delta E> = -\frac{\pi\rho\,Z\,\beta^3\,mc^3}{(1-\beta^2)}\int_{\theta_1}^{\theta_2}\theta^2\,\sigma(\theta)\sin\theta\;d\theta \qquad (1{\cdot}37)$$

Comparing this with Eq. (1.19) we note the appearance of $(1-\beta^2)$ in the denominator here. Carrying out the integration and setting $\theta_2/\theta_1 = \lambda_D/b_{min} = \lambda_D p/\hbar$ we obtain

$$<\Delta E> = -\frac{4\pi\rho\,Z\,r_o^2\,mc^3}{\beta}\;ln\,(\lambda_D\,p/\hbar) \qquad (1.38)$$

Defining $E' = E/mc^2$ we have

$$\frac{dE'}{dt} = -\frac{4\pi\rho\,Z\,r_o^2\,c}{\beta}\;ln\,(\lambda_D\,p/\hbar) \qquad (1.39)$$

for the energy loss rate in a fully ionized hydrogen plasma.*

In neutral material the log term is more complicated since it now represents the maximum and minimum possible energy transfers. The exact result is the well-known Bethe-Bloch formula [Rossi, 1952].

$$\frac{dE'}{dt} = -\frac{2\pi\rho\,Z\,r_o^2\,c}{\beta}\left[\;ln\left(\frac{\pi^2\,m^2\,c^4}{(1-\beta^2)^{3/2}\,I^2\,(Z)}\right) - 2{\cdot}9\;\right] \qquad (1.40)$$

I (Z) is the ionization potential, averaged appropriately over all electrons.

As in the case of scattering we define an *effective density for energy loss* ρ_E, through

$$\rho_E\,ln\,(\lambda_D/b_{min}) = \sum_i \rho_i\left\{N_i\;ln\,(\lambda_D/b_{min}) + \tfrac{1}{2}\,(Z_i - N_i)\left[\;ln\left(\frac{\pi^2\,m^2\,c^4}{(1-\beta^2)^{3/2}\,I^2\,(Z_i)}\right) - 2{\cdot}9\;\right]\right\} \qquad (1{\cdot}41)$$

assuming $ln\,(\lambda_D/b_{min}) = 23$.

* This result may also be derived on the basis of plasma dynamics (Gasiorowicz, Neuman and Riddell, 1956).

For fully ionized hydrogen $Z = N = 1$ and

$$\rho_E = \rho(H^+). \tag{1.42.1}$$

For neutral hydrogen $I(Z) = 14{\cdot}9$ [Rossi, p. 23]. For $\beta \sim 0{\cdot}8$ and $ln\ (\lambda_D / b_{min}) = 23$ we find

$$\rho_E(H) = \frac{10{\cdot}9}{23}\ \rho(H) = .47\ \rho(H) \tag{1.42.2}$$

For singly ionized oxygen, assuming $I \sim 100$ ev we find

$$\rho_E(O^+) = 3{\cdot}74\ \rho(O^+) \tag{1.42.3}$$

For neutral oxygen, assuming $I \sim 80$ ev (the measured value for air) [Rossi, p. 22] we find

$$\rho_E(O) = 3{\cdot}22\ \rho(O) \tag{1.42.4}$$

Table 1·2 summarizes these results.

TABLE 1·2

Multiply true density by appropriate conversion factor to obtain effective energy loss density, ρ_E.

Material	Conversion Factor
Fully ionized hydrogen	1·0
Neutral hydrogen	0·47
Singly ionized oxygen	3·74
Neutral oxygen	3·22

Finally, we briefly discuss *simultaneous* deflection and energy-loss. Consider a fast electron moving in a *homogeneous* plasma. The rate of energy dissipation will be independent of the electron's direction of motion. However, the rate of deflection will increase as the electron slows down. We should like to compare the times $T(\phi)$, the mean time required for deflection through an angle ϕ, and $\tau(\eta)$, the mean time required for the energy to decrease to $\eta\ E_{initial}$, $\eta < 1$.

Define

$$A = 4\pi r_o^2\ c\ ln\ (\lambda_D\ p/\hbar). \tag{1.43}$$

Then Eqs. (1.35) and (1.39) may be rewritten as

$$< \theta^2 > = 2A\rho_s\ \frac{(1 - \beta^2)}{\beta^3}\ \frac{}{} \tag{1.44}$$

and

$$\frac{dE'}{dt} = - A\rho_E/\beta \tag{1.45}$$

Assume $\beta^2 << 1$. Then (1.44) becomes

$$< \theta^2 > = \frac{d}{dt}\phi^2 = 2A\rho_s/\beta^3 \tag{1.46}$$

Also

$$E' = \frac{E}{mc^2} = \tfrac{1}{2}\beta^2,$$

$$\frac{dE'}{dt} = \beta \frac{d\beta}{dt} \tag{1.47}$$

Inserting this into (1.45)

$$\beta^2 \frac{d\beta}{dt} = - A\rho_E \tag{1.48}$$

Since the atmosphere is homogeneous we may integrate (1·48) without regard for the effect of deflection:

$$\beta_f^3 - \beta_i^3 = - 3A\rho_E t \tag{1.49}$$

or

$$\beta^3(t) = \beta_i^3 - 3A\rho_E t \tag{1.50}$$

Now,

$$\eta = \frac{E(t)}{E_i} = \frac{\beta^2(t)}{\beta^2_i}$$

or

$$\beta^3(t) = \eta^{3/2}\beta_i^3$$

Therefore,

$$3A\rho_E t(\eta) = \beta_i^3 - \beta^3(t) = \beta_i^3\left[1 - \eta^{3/2}\right]$$

and

$$\tau(\eta) = \frac{\beta_i^3}{3A\rho_E}(1 - \eta^{3/2}) \tag{1.51}$$

This is the time it takes for the electron to lose a fraction $(1 - \eta)$ of its initial energy.

We next integrate (1.46), taking into account the variation of β. Insert (1.50) into (1.46) and integrate

$$\phi^2 = 2A\rho_s \int_0^{T(\phi)} \frac{dt}{\beta_i^3 - 3A\rho_E t}$$

$$= \frac{2\rho_s}{3\rho_E} \ln \left(\frac{\beta_i^3}{\beta_i^3 - 3A\rho_E T(\phi)} \right)$$

Hence

$$T(\theta) = \frac{\beta_i^3}{3A\rho_E} \left[1 - \exp \left(- \frac{3\rho_E}{2\rho_s} \phi^2 \right) \right] \tag{1.52}$$

But, from (1.51), the facter in front of the square bracket in (1.52) is related to $\tau(\eta)$, giving

$$T(\phi)/\tau(\eta) = \left[1 - \exp \left(- \frac{3\rho_E}{2\rho_s} \phi^2 \right) \right] / \left[1 - \eta^{3/2} \right] \tag{1.53}$$

Eor a given atmosphere ρ_E / ρ_s is fixed. For fully-ionized hydrogen we find $\rho_E / \rho_s = \frac{1}{2}$ while for neutral hydrogen $\rho_E / \rho_s = 1{\cdot}17$. For an oxygen atmosphere the Z^2 – dependence of scattering reduces this ratio greatly, being 0·23 for O^+, 0·22 for O.

Take $\rho_E / \rho_s = \frac{1}{2}$ (i. e., H^+) and take $\eta = 0{\cdot}10$. Then, for $\phi = \pi/2$:

$$T(\phi = \pi/2)/\tau(\eta = 1/10) = 0{\cdot}87.$$

Hence, *the times for full-deflection and for loss of almost all energy are about equal.*

We have regarded ϕ and η as independent variables, which is permissible if we simply ask for the time needed to scatter through ϕ degrees without inquiring as to the value of η when ϕ is reached. However, ϕ and η are related through (1.51) and (1.52). That is, if we start an electron off with energy $E_i \lesssim mc^2$, then after a time t it will have slowed down to $E(t) = \eta(t) E_i$ and will have, on the average, been deflected through an angle $\phi(t)$, where (1.51) is an implicit equation for $\eta(t)$. Equating (1.51) and (1.52)

$$\frac{\beta_i^3}{3A\rho_E} \left[1 - \eta(t)^{3/2} \right] = \frac{\beta_i^3}{3A\rho_E} \left[1 - \exp \left(- \frac{3\rho_E}{2\rho_s} \phi^2(t) \right) \right]$$

or

$$\eta(t) = e^{-\frac{\rho_E}{\rho_s} \phi^2(t)} \tag{1.54}$$

For $\rho_E / \rho_s = \frac{1}{2}$ (ionized hydrogen) this result shows that a deflection of 90° is accompanied by the loss of slightly more than 90% of the initial energy. Values of η vs ϕ are given in Table 1.3.

Now consider a highly relativistic electron, $\beta \simeq 1$. Radiative effects shall be ignored. Eq. (1.44) becomes

$$< \theta^2 > = 2A\rho_s (1 - \beta^2)$$

But

$$(1 - \beta^2) = \left(\frac{mc^2}{mc^2 + E} \right)$$

Therefore

$$< \theta^2 > = 2A\rho_s \left(\frac{mc^2}{mc^2 + E} \right)^2 \tag{1.55}$$

Eq. (1.45) now reduces to

$$\frac{dE'}{dt} = - A\rho_E = \text{constant} \tag{1.56}$$

Integrating (1.56)

$$E(t) = E_i - A\rho_E mc^2 t \tag{1.57}$$

Insert (1.57) into (1.55)

$$< \theta^2 > = \frac{d\phi^2}{dt} = 2A\rho_s \left(\frac{mc^2}{mc^2 + E_i - A\rho_E mc^2 t} \right)^2 \tag{1.58}$$

Integrate (1. 58)

$$\phi^2(t) = 2 \frac{\rho_s}{\rho_E} (mc^2) \left\{ \frac{1}{mc^2 + E_i - A\rho_E mc^2 T} - \frac{1}{mc^2 + E_i} \right\} \tag{1.59}$$

Replace $E_i - A\rho_E mc^2 T$ by E (T) and divide top and bottom by E_i. The result is

$$\phi^2 = 2 \frac{\rho_s}{\rho_E} \frac{mc^2}{E_i} \left\{ \frac{1}{\frac{mc^2}{E} + \eta} - \frac{1}{\frac{mc^2}{E_i}} + 1 \right\} \tag{1.60}$$

In Table 1.3 we give ϕ vs η for ionized hydrogen and assuming $E_i = 10\, mc^2$. It will be observed, by comparison with the non-relativistic result, that for a given value of η the *rms* deflection is substantially smaller in the relativistic case than in the non-relativistic case. This effect is the basis for the asertion that scattering becomes less important relative to energy-loss at high energy.

TABLE 1·3

Root-mean-square deflection angle *vs* relative energy-loss for electron in ionized hydrogen.

$E_f/E_i \equiv \eta =$	·9	·8	·7	·6	·4	·2	·1
$\phi°$ ($E_i >> kT$)	18	27	34	41	55	72	87
$\phi°$ ($E_i = 10\, mc^2$)	7·8	11·5	15·0	18·5	26·8	40·0	51·8

2. APPLICATION TO TRAPPED PARTICLES

Charged particles spiralling in a static magnetic field whose scale of inhomogeneity is large compared to the gyroradius move in such a way as keep

$$\sin^2 \alpha/B = \text{constant} \tag{2.1}$$

Here α is the pitch angle, i. e., the angle between the velocity vector and the local magnetic field B. As a consequence a particle tends to be reflected as it penetrates into a region of increasing field strength.

For particles trapped in the earth's magnetosphere, the Coulomb interactions experienced on a *single* north-south oscillation cause only a small perturbation in a particle's energy or equatorial pitch angle. It is therefore possible to represent the system by a distribution function n (E, μ, r_e) which is the unidirectional differential concentration (particles $kev^{-1}\ cm^{-s}\ ster^{-1}$) referred to a given spiral orbit or to a line of force and equatorial pitch angle α_e. Here $\mu = \cos \alpha_e$ and r_e is the equatorial geocentric distance of the line of force in a dipole field. Further, as a consequence of the negligible loss of energy in a *single* oscillation and through the application of Liouvilie's theorem, the unidirectional intensity $n\beta c$ is a constant everywhere along a spiral path.

In a static magnetic field particles are lost from the system either by (a) losing energy until they are undetectable or (b) changing their equatorial pitch angle until their mirror point falls within the more dense layers of the atmosphere, say below 1200 km, whereupon they are absorbed.

To a first approximation the equilibrium concentration is given by $n = q\mathrm{T}$, where q is the injection rate and T is the lifetime. In this rough approximation a lifetime on the order of the mean time for deflection through one radian (Eq. 1.52) or the time for loss of a large fraction of the initial energy (Eq. 1.51) will suffice. In table 2.1 we give lifetimes for a 300 kv electron trapped at various distances from the earth.

TABLE 2·1

Lifetime for loss of 90 per cent of energy $\mathrm{T_E}$ for 300 kev electron and lifetime for scattering through $\sim 60°$, $\mathrm{T_s}$. (Equatorial pitch angle 60°) $\bar{\rho}_E$ is effective density averaged over orbit. A quiescent magnetic field is assumed.

r_e/R	$\bar{\rho}_E$ (cm^{-3})	$\mathrm{T_E}$ (years)	$\mathrm{T_s}$ (years)
1·5	$\sim 10^5$	$\sim$ 0·12	$\sim$ 2·8
2	$2{\cdot}1 \times 10^3$	6·7	15·6
3	$5{\cdot}2 \times 10^2$	26·2	62·6
4	$2{\cdot}3 \times 10^2$	59	141
5	$1{\cdot}2 \times 10^2$	118	282

A more precise treatment is possible by employing the Fokker-Planck equation, which expresses the rate of change of the distribution function under the influence of small perturbations. In adapting the Fokker-Planck equation to the

dipole field of the earth, the deflections introduced by scattering at an arbitrary point along the orbit must be properly transformed into changes of μ. The proper transformation was found by MacDonald and Walt (1961) and independently by Wentworth (Wentworth, 1963). The resulting equation is

$$\frac{\partial n\,(E,\mu,t)}{\partial t} = -\frac{\partial}{\partial E}\left[n \frac{\partial E}{\partial t} \right] + \frac{D}{\mu s\,(\mu)} \frac{\partial}{\partial \mu}\left[(1-\mu^2)\,\mu s\,(\mu) \frac{n}{\partial \mu} \right] + \bar{q}\,(E,\mu,t) \qquad (2.2)$$

Here

$$D = \tfrac{1}{4} < \theta^2 >, \qquad (2.3)$$

(cf. Eq. 1.28), with ρ_s set equal to *one half the equatorial value* of ρ_s (Wentworth, 1960). The rate of energy loss is that given by Eq. (1.39) with ρ_E set equal to $\bar{\rho}_E$, the average over the spiral path. The quantity $s\,(\mu)$ is the dimensionless length of the spiral path, expressed in terms of r_0. The term $\bar{q}$ is the injection rate, averaged over the spiral path.

Solutions of Eq. (2.2) have been given (Lenchek, Singer and Wentworth, 1961 ; Walt and MacDonald, 1961) for the case of injection by beta decay of slow neutrons issuing from the atmosphere, the so-called neutron albedo from cosmic ray interactions.

Valuable insight into the behavior of trapped electrons may be gained by considering the effects of energy loss and pitch angle diffusion separately.

Suppose an electron's pich angle does not change but it loses energy by collisions. The second term on the right of Eq. (2.2) is thus set equal to zero and, assuming equilibrium, the equation may be integrated to give

$$n\,(E,\mu) = \frac{1}{|\,\partial E, \partial t\,|} \int_E^\infty \bar{q}\;E\;\mu)\;dE_i \qquad (2.4)$$

Since $\partial E/\partial t$ is proportional to $\bar{\rho}_E\,(\mu)$, we see that the equilibrium concentration in a given orbit is inversely proportional to the atmospheric density averaged over the orbit. If the energy dependence of $\bar{q}$ has the form $E_i^{-\gamma}$ then, for non-relativistic energies, the energy dependence of $n\,(E)$ will be $E^{1.5-\gamma}$, giving an intensity proportional to $E^{2-\gamma}$.

Finally, if we suppose that an electron only scatters without losing energy we may drop the first term on the right of Eq. (2.2). Assuming the source has the form $Q(E)\,f(\mu)$ we find that the equilibrium energy spectrum is $Q(E)\,\beta^2\,(1-\beta^2)^{-1}$. The angular dependence of n is obtained by integrating the remaining equation, subject to the boundary condition $n\,(\mu_0) = 0$, where μ_0 is the parameter belonging to an orbit which mirrors at the "transition altitude" ($\sim$ 1200 km) marking the boundary between the inner magnetosphere (where oxygen is the dominant constituent) and the other magnetosphere (where hydrogen is dominant).

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FREE ENERGY CONSIDERATION IN TWO ELECTRON TRANSFER REACTIONS BETWEEN TWO IONS IN SOLUTION

By

B. KRISHNA *and* B. P. SINHA

Physical Chemistry Laboratories, University of Allahabad, Allahabad

When a collision between two ions involving electron transfer occurs in solution, the actual process is very complicated particularly if the solvent molecule gets associated with colliding ions. However, of late, there have been attempts by Marcus,[1] Marcus, Zwolinski and Eyring[2], Weiss[3], Laidler[4] and others to define more exactly the process of formation of activated complex. This in general is assumed to be formed in two ways :

(*a*) *Non-adiabatic electron transfer* — This corresponds to very weak interaction of the two states according to which the free energy of activation is split up into three parts.

$$\triangle F^* = \triangle F^*_{repul} + \triangle F^*_{reorg} - RT \log \kappa$$

Where $\triangle F^*$ is the total apparent free energy of activation, $\triangle F^*_{repul}$ is part due to the repulsion of ions in the activated complex, $\triangle F^*_{reorg}$ is the Franck-Condon reorganisation free energy and κ is the transmission coefficient which represents the probability that the system will remain on the lower surface on the potential energy diagram.

(*b*) *Adiabatic transfer*—This is further subdivided into—

(a) *Weak interaction* :—In this case the electronic interaction between the reactants in the activated complex is enough to allow it to remain on the lower surface of the potential energy diagram (*i.e.* $\kappa \approx 1$).

(b) *Strong interaction* :—This is the case which occurs in ordinary chemical reactions, in which covalent bonds are ruptured and new bonds are formed simultaneously. For instance in redox reactions occurring through the transfer of covalent bonded atom like oxygen atom or electron transfer in which metal ions are coupled strongly by inner sphere bridging ligands.

Most of their conclusions are, however, based upon the examples taken from reactions involving one electron transfer and there does not appear to be any general conclusion involving multiple electron transfer. Some of the observations that we have made relate to processes involving two electron transfer.

It is well known relation that the speed of a reaction is determined by the free energy of activation and not by the net free energy change of the reaction *i.e.*

$$k = A\, e^{-\triangle F^*/RT}$$

where k is the rate constant, $\triangle F^*$ is the free energy of activation and A is a constant. But we have found that when a reaction between two ions in solution results in the transfer of two electron from one ion to another, the total free energy decrease also appears to be the dominant factor. The present authors have studied

a number of reactions involving two electron transfer from re ductant to oxidant. To illustrate the above point of view, we consider three reactions namely the oxidation of thallous (I) ion by ceric (IV) ion, stannous (II) ion by ferric (III) ion and stannous (II) by ceric (IV) ion. All these reactions involve two electron transfer reductant to oxidant. We have studied the kinetics of these reactions in great detail[5,6]. The reaction between ceric ion and thallous ion is extremely slow so much so that for all practical purposes, the rate appears to be zero. However in presence of a suitable concentration of platinic chloride catalyst, the reaction proceeds with measurable speed and hence we have employed it as catalyst. The oxidation of stannous ion by ferric ion is quite fast while that of stannous ion by ceric ion is the fastest. The rate constant of the three reactions mentioned are (*a*) $k = 0{\cdot}01445$ Min^{-1}, (*b*) $k = 0{\cdot}4390$ litres/gm. eq. Min., (*c*) $k = 42{\cdot}57$ litres/gm. eq. Min. We now calculate the equilibrium constant for these reactions on the basis of redox potentials[7].

Electrodes	E_o in volts at 25°C
$Ce^{++++}/Ce^{+++}/Pt$	1·45
$Tl^{+++}/Tl^{+}/Pt$	1·23
$Fe^{+++}/Fe^{++}/Pt$	0·77
$Sn^{+++}/Sn^{++}/Pt$	0·15

Now consider the reaction between ceric ion and thallous ion

$$2\,Ce^{++++} + Tl^{+} \rightleftharpoons 2\,Ce^{+++} + Tl^{+++}$$

The equilibrium constant for this reaction is given by

$$\log_e K = \frac{2F}{RT}\ (1{\cdot}45 - 1{\cdot}23)$$

$$\log_{10} K = \frac{2}{0{\cdot}059} \times 0{\cdot}22$$

$$K = 2{\cdot}864 \times 10^{7}$$

Similarly the reaction,

$$2\,Fe^{+++} + Sn^{++} \rightleftharpoons 2\,Fe^{++} + Sn^{++++}$$

$$K = 1{\cdot}023 \times 10^{21}$$

and for the reaction

$$2\,Ce^{++++} + Sn^{++} \rightleftharpoons 2\,Ce^{+++} + Sn^{++++}$$

$$K = 1{\cdot}175 \times 10^{44}$$

Since the equilibrium constant of a reaction is related to standard free energy change by the equation

$$-\triangle F^{o} = RT \log_e K$$

where ΔF° represents the standard free energy change. Employing this equation, the standard free energy calculated for the above mentioned reactions from the values of equilibrium constants are—

(*i*) $2\,Ce^{++++} + Tl^{+}$ ... $-\Delta F^{\circ} - 10{\cdot}18$ k Cal.

(*ii*) $2\,Fe^{+++} + Sn^{++}$ ... $-\Delta F^{\circ} - 28{\cdot}75$ k Cal.

(*iii*) $2\,Ce^{++++} + Sn^{++}$ ... $-\Delta F^{\circ} - 60{\cdot}05$ k Cal.

Based upon these calculations we find that greater the free energy change in such type of reactions *i.e.* (in two electron transfer reactions in aqueous solution) the greater will be the speed of the reaction. It is thus most likely that in reactions in which one reactant donates a pair of electron and the other receives only one (atom for atom), the magnitude of net free energy decrease may be employed as a rough criterion for comparing the rate constants but at the same time it should always be kept in mind that comparison should be made, as far as possible, under identical conditions *i.e.*, in the same medium and with same type of compounds.

One of us (B. P. S.) is grateful to the University Grants Commission, Government of India for the award of a senior research fellowship.

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SZILARD—CHALMERS' REACTION IN ELEMENTARY IODINE

By

H. J. ARNIKAR* *and* D. K. SHARMA

Laboratory of Physical & Nuclear Chemistry, University of Banaras

ABSTRACT

An application of the (n, γ) recoil principle to the separation of isotopic products from targets of *elementary* substances does not appear to have been reported earlier. A value of about 1·2 eV for the I—I bond energy suggests that this bond should be at least as readily susceptible to rupture during (n, γ) recoil as the bond C—I of energy 2·0 eV. This expectation has been borne out by our results on the application of the Szilard-Chalmers technique to elementary iodine dissolved in organic solvents. Following are amongst the results of interest.

(1) A 5—100 time greater specific activity results in the aqueous extract compared with the residual organic layer while the distribution of *total* iodine, (active + inactive) between the two phases corresponds to the usual value of partition coefficient.

(2) The over-all yield of I^{128} is relatively greater (~ 1·5 times) for irradiation in aromatic than in aliphatic media, under otherwise same conditions.

(3) The proportion of charged particles, if any, in the active products is negligible unlike in the irradiation of halogen *compounds* where about 30% of the activity collects on charged plates, as shown in our earlier work on MeI, EtI, PhI and PhBr.

INTRODUCTION

An application of the (n, γ) recoil principle to the separation of isotopic products from targets of *elementary* substances does not appear to have been reported earlier. A value of about 1·2 eV for the I—I bond energy suggests that this bond should be at least as readily susceptible to rupture during (n, γ) recoil as the bond C—I of energy 2·0 eV. This expectation has been borne out by our results on the extraction of I^{128} into the aqueous phase following the application of the Szilard—Chalmers technique to elementary iodine dissolved in organic solvents.

We present here some of our results.

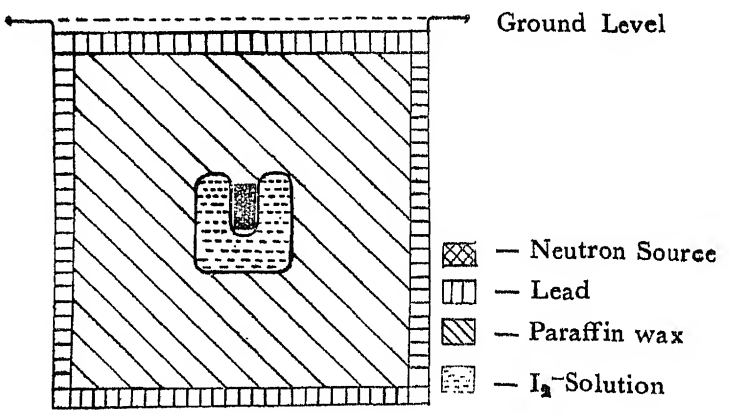

Fig. 1. Irradiation system

*Present address—University Professor of Chemistry, University of Poona.

EXPERIMENTAL

5 gms of twice sublimated pure iodine were dissolved in 200 ml. of the solvent CCl_4, C_6H_6, $CHCl_3$ and $C_6H_5.CH_3$ and subjected to irradiation by slow neutrons from a 300 mg source of Ra + Be plunging in the centure of the liquid with adequate paraffin surrounding the system for thermalisation of the neutrons. (See Fig. 1).

The irradiation was continued for a period of 3 hours which corresponds roughly to 6 half lives of I^{128}. The total activity produced was measured immediately in an aliquot part of the solution by a liquid counter and the specific activity calculated by determining chemically the total mass of iodine present. In another aliquot fraction, 20 ml. of water were added to 60 ml. of solution and shaken. The mixture was allowed to settle down for 10 minutes till the two layers separated. Total and specific activity in the two phases were determined separately. Results are shown in Table I.

DISCUSSIONS

The I—I bond energy being of the order of 1·2 eV, it may be expected to break easily during the (n, γ) recoil of one of the atoms. The date of Table I on the concentration of radio iodine in the aqueous layer of a relatively high specific activity, confirms this. A successful application of the Szilard Chalmers' reaction to *elementary* iodine, does not appear to have been reported hitherto Following are among the more important findings of the above series of experiments.

(1) A 5—100 times greater specific activity results in the aqueous extract compared with the residual organic layer while the distribution of *total* iodine, (active + inactive) between the two phases corresponds to the usual value of the partition coefficient.

(2) The over-all yield of I^{128} is relatively greater ($\sim$ 1·5 times) for irradiation in aromatic than in aliphatic media, under otherwise same conditions.

(3) The proportion of charged particles, if any, in the active products is negligible unlike in the irradiation of halogen *compounds* where about 30% of the activity collects on charged plates, as shown in our earlier work on MeI, EtI, PhI and PhBr.

A unique characteristic of the present Szilard-Chalmer's reaction in elementary iodine is the formation during the (n, γ) recoil-rupture of two *atomic* fragments as the first products identical with each other, except for the very slight isotopi c mass difference and, of course, radioactivity.

$$I^{127} - I^{127} + n \rightarrow (I^{127} - I^{128})^{*} \rightarrow I^{127} + I^{128} + \gamma$$

This is very unlike Szilard-Chalmers' reactions studied earlier on combined halogens where the first products of rupture are very dissimilar, the rest of the target molecule constituting the inactive fragment.

The two isotopic fragments of iodine resulting in the primary reaction share nearly equally the excess recoil energy after the bond rupture. Being thus too 'hot' for a direct recombination, these atoms may be expected to remain as free-radicals and hence can pass readily into the aqueous phase, as in classical Szilard-Chalmers' reaction on halogen compounds. Our experiments confirm this. The resulting aqueous and organic solvent layers should be of same specific activity, as the two isotopic fragments are formed in equal numbers as the primary products of rupture. Experimental findings, however, are different. The observed specific activity of the aqueous phase is much higher than that of the solvent phase, in the ratio of 5 to 1 in the case of benzene and toluene, and 100 to 1 in the case of carbon tetrachloride and chloroform, though in all cases, the net distribution of total iodine (active and inactive) conforms to usual partition coefficient values.

TABLE I

Target 5 g of I_2 dissolved in 200 ml. of	Total I_2 present in 60 ml. of solution (a)	Total activity produced in 60 ml. (b)	Specific activity produced initially (b/a)	After extraction with water (20 ml. of water + 60 ml. of soln.). Activity in 20 ml. of water layer (c)	Activity in 60 ml. of solvent layer (d)	Amt. of I_2 in 20 ml. of water layer (e)	Amt. of I_2 in 60 ml. of solvent layer (f) = (a) − (e)	Sp. activity in water layer (c/e)	Sp. activity in solvent layer (d/f)
	g	c/m	$\times 10^{-3}$	c/m	c/m	g. $\times 10^{3}$	g	$\times 10^{-3}$	$\times 10^{-3}$
Benzene ...	1·5011	6120	4·08	20	6080	0·89	1·5002	22	4·05
Toluene ...	1·4862	6180	4·16	30	6130	1·27	1·4849	24	4·13
Carbon—tetrachloride ...	1·4940	4350	2·91	1220	3130	5·33	1·4887	230	2·10
Chloroform ...	1·5090	4650	3·08	1020	3630	3·52	1·5055	290	2·43

This excess specific activity of the aqueous phase implies secondary reactions leading to a lower retention of the active species in the irradiation medium. It is suggested that this may be due to a slightly longer mean life of the active free radical (I^{128}) than for the inactive counterpart. This agrees with the finding that the excess specific activity of the aqueous phase diminishes rapidly with increasing time interval between the end of irradiation and the addition of water for separation.

Results of Table I reveal a marked difference in regard to the ratio of specific activity of aqueous phase to that of the solvent. This ratio is about 100 in the case of CCl_4 and $CHCl_3$ which give purple solution of iodine, while the ratio is only 5 in the case of C_6H_6 and $C_6H_5CH_3$ which give brown solutions. In solvents of the latter type, iodine is known to form complexes of the 1:1 type of low heat of formation of the order of one KCal/Mole [1] The concurrent breaking of these during the recoil of the iodine atoms provides an additional fragment of rupture, the solvent molecule, which, being much lighter, will carry a greater fraction of the excess recoil energy, leaving the iodine fragments correspondingly less 'hot' than in the straight rupture of an I—I bond. A greater recombination, and hence higher retention, is thus to be expected in the case of a 3-fragment ruputre leading to a relatively smaller excess of specific activity in the aqueous phase as observed.

The 50% higher total isotopic yield obtaining in the case of aromatic over aliphatic solvents, used as media of irradiation, appears to be a result anticipatable from the general conditions of irradiation. The (Ra + Be) source at the centre of the target, is one of fast neutrons, the necessary thermalization being effected by external reflection from the surrounding paraffin, (See Fig. 1), the target is thus subject to bombardment mainly by slow neutrons from outside and to a limited extent by fast neutrons directly from the source at the centre. Media rich in hydrogen (as C_6H_6 and $C_6H_5CH_3$) would be able to function as relatively better internal moderators in comparison to those having no hydrogen (as CCl_4) or only a low content of it (as $CHCl_3$). The proportion of fast neutrons is less by internal moderation in the case of iodine dispersed in aromatic than in aliphatic media, hence a greater yield of the slow neutron reaction product in the former case as observed. The presence of an appreciable flux of effective fast neutrons is borne out by the reaction Cl^{35} $(n, \alpha)P^{32}$ actually observed when pure carbon tetrachloride is irradiated for prolonged periods of 2—3 days under otherwise same conditions.

The other significant difference of the Szilard-Chalmers' reaction in elementary iodine is the non-formation of charged particles of the active species separable in an electric field. This is unlike our earlier work[2,3] on (n,γ) recoil in halogen compounds as EtI, MeI, PhI and PhBr where about 30% of the active products could be collected on charged plates, though the precise mechanism of the transformation of a part of the free radicals initially produced into ions of both signs, as observed, still remains to be understood. The possibility of photoionization of the free radicals by the gamma of the (Ra + Be) source or of the (n, γ) reaction does not appear to be adequate as evidenced by its inoperation in the present case of Szilard Chalmer's reaction on elementary iodine.

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CHEMICAL INTERACTION BETWEEN HYDROCARBONS AND PICRIC ACID IN THE SOLID STATE

By

R. P. RASTOGI,* PARMJIT S. BASSI *and* S. L. CHADHA

Chemistry Department, Panjab University, Chandigarh-3

ABSTRACT

The chemical reaction between naphthalene and picric acid has been investigated by a new technique which involves the study of the movement of the coloured boundary at the interface of the reactants in the solid state kept side by side. The reaction depends on the particle size. For particles of 50 mesh the energy of activation and entropy of activation are 11·36 kcal. and 21·46 cal/mole/deg. respectively.

It appears from the data that the phase-boundary processes are very rapid and equilibrium is established at the boundaries during the entire course of reaction and the solid-state diffusion in the product layer is alone rate determining. This diffusion may be structure-sensitive. The experimental data are not yet adequate to settle this point. Some comments on the mechanism of diffusion have also been made.

1. INTRODUCTION

When two reacting solids are kept in contact, the reaction usually takes place at the boundary within a short interval. Further reaction depends on the ease of diffusion through the product layer. The diffusion of molecules to the zone of reaction is quite easy in gaseous and liquid phases. In solid phase, it is relatively a much difficult process and is not much understood. A considerable amount of information about the solid-state diffusion through the migration of lattice defects has been accumulated during recent years but similar information about other modes of diffusion is not available. On account of these difficulties, chemical reactions in the solid-state offer an exiting field. The present paper makes an attempt to describe the mechanism of chemical interaction between naphthalene and picric acid in the solid state.

2. EXPERIMENTAL

Naphthalene picrate is formed at the interface between solid naphthalene and solid picric acid. The rate of such a reaction was followed by noting the thickness of the reaction zone at various time intervals as described in a recent communication.[1] The only difference in the procedure followed was that particles of different meshes were used for investigation since it was discovered that the rate of reaction depends on particle size. Rate of reaction at 35 ± 1°C for particles of 25 mesh, 50 mesh, 100 mesh and 200 mesh was studied. In addition the reaction rate measurements were made at different temperatures for particles of 50 mesh. The results are given below. Naphthalene purified by sublimation in vacuum and picric acid purified by fractional crystallization with ethanol were used for the investigation. The melting-point of naphthalene was 80·3°C and that of picric acid was 121·4°C.

*Present address : Department of Chemistry, University of Gorakhpur, Gorakhpur.

The results are recorded in Tables I and II.

3. RESULTS

TABLE I.

Effect of particle size on the reaction rate at 35±1°C

(a) Particle size 25 mesh.		(b) Particle size 50 mesh	
Time t (hours)	Thickness of the reaction zone ξ (mm)	Time t (hours)	Thickness of the reaction zone ξ (mm)
0·0	0·0	0·0	0·0
0·88	1·88	1·27	1·62
1·42	2·30	1·8	1·82
14·5	5·28	19·0	4·50
22·2	5·92	27·0	5·05
53·0	7·72	67·0	6·55
58·9	7·90	75·0	6·75
76·5	8·50	91·0	7·20
106·25	9·18	116·0	7·80
		140·0	8·20

(c) Particle size 100 mesh.		(d) Particle size 200 mesh.	
Time t (hours)	Thickness of the reaction zone ξ (mm)	Time t (hours)	Thickness of the reaction zone ξ (mm)
0·0	0·0	0·0	0·0
1·58	1·30	2·69	1·20
2·3	1·52	19·0	2·78
31·25	4·20	27·0	3·20
67·0	5·38	67·0	4·30
75·0	5·60	75·0	4·40
91·25	6·00	91·0	4·80
124·0	6·50	116·0	5·20
145·0	6·80	140·0	5·60

TABLE II

Effect of temperature on reaction rate for particles of 50 mesh.

(a) Temperature 45±1°C	
Time t (hours)	Thickness of the reaction zone ξ (mm)
0·0	0·0
1·9	2·7
3·15	3·3
22·4	6·5
75·5	9·0
82·2	9·16
107·5	9·82
152·7	10·80

(b) Temperature 61±1°C	
Time t (hours)	Thickness of the reaction zone ξ (mm)
0·0	0·0
2·68	3·5
14·5	6·4
18·2	6·9
45·0	8·9
67·1	9·5
119·0	11·44
168·0	12·51

(c) Temperature 35±1°C

as given in Table (b).

The above results are plotted in Figures (1) and (2).

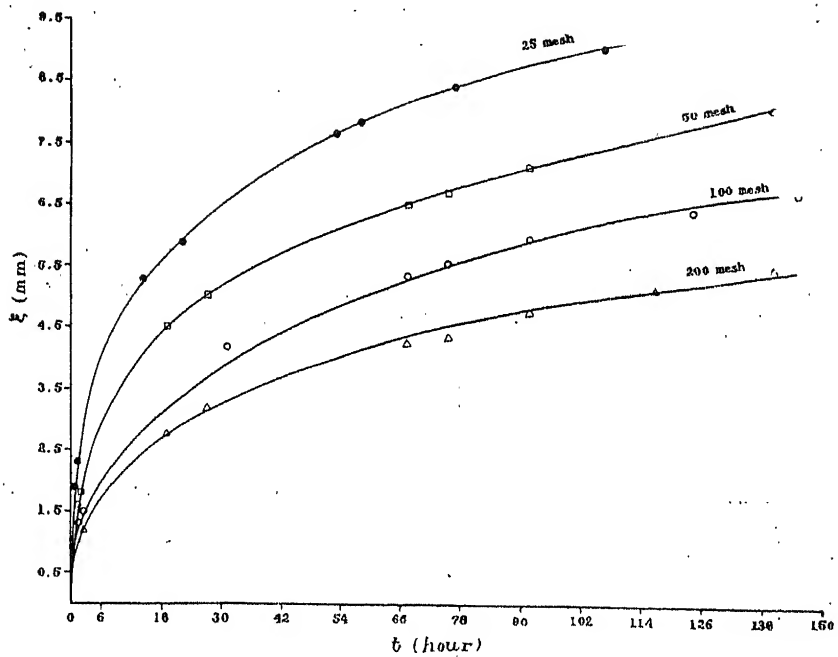

Fig. 1. Effect of particle size on the reaction rate at 35 ± 1°C.

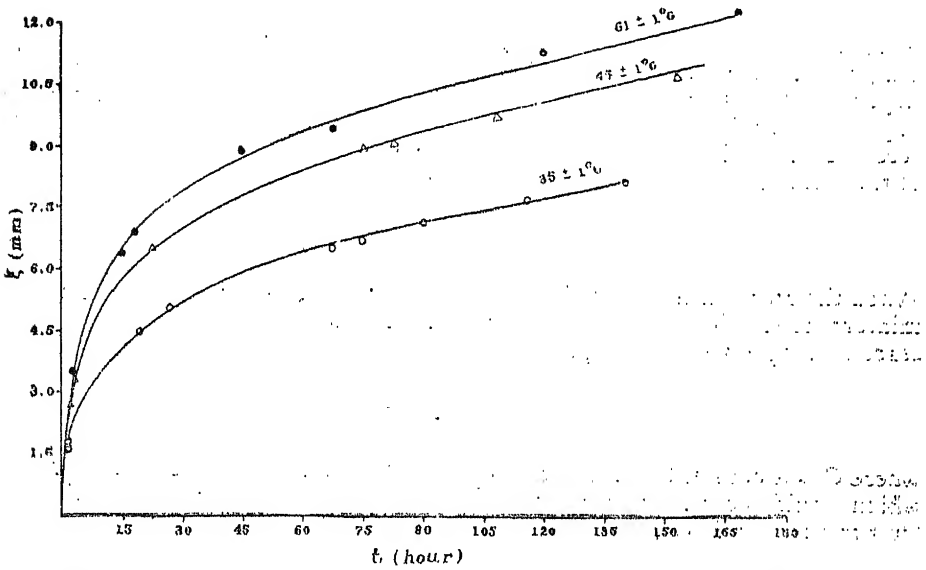

Fig. 2. Effect of temperature on reaction rate for particles of 50 mesh.

4. DISCUSSION

Fig. 1. shows that the reaction rate is strongly dependent on particle size. Accordingly for measurement of reaction rate at different temperatures a definite particle size was chosen. From the general features of the reaction it appears that the phase-boundary process is much faster and solid-state diffusion is the rate determining step. From Fick's law of diffusion we have, J, the mass flowing per unit time given by,

$$J = D. \frac{\partial c}{\partial x} \tag{1}$$

where $\partial c/\partial x$ is the concentration gradient and D is the diffusion co-efficient of the reacting species. In the particular reaction under study, only naphthalene diffuses through the product layyer whereas picric acid does not. Thus D is simply the diffusion co-efficient of naphthalene in the solid. Now,

$$J = \rho. \frac{d\xi}{dt} \tag{2}$$

where ρ is the density of diffusing substance through unit-cross section of diffusion zone and $\frac{d\xi}{dt}$ is the rate of growth of the product layer. Accordingly, we can write equation (1) as,

$$\rho. d\xi/dt = D. \partial c/\xi \tag{3}$$

Since on the picric acid side of the reaction zone, the concentration of naphthalene is zero, hence ∂c would be constant. Thus,

$$d\xi/dt = k/\xi \tag{4}$$

where k is a constant and is equal to $D.\partial c/\rho$. Since both D and ρ depend on temperature, evidently k would be a function of temperature. It would largely depend on the strongly temperature dependent D. Since the co-efficient of volume expansion of solids is small, we may expect ρ not to vary much with the temperature. This would mean that k would vary with temperature in a manner analogous to the diffusion co-efficient D. Integration of equation (4) yields,

$$\xi^2 = 2. kt \tag{5}$$

When the reaction is initiated at any temperature, the temperature of the reaction mixture rises almost instantaneously from which it gradually decreases as the reaction progresses. It is ligitimate to assume that,

$$k = C. \exp.(-E/RT) \tag{6}$$

where C is a constant and E is the energy of activation, a much larger part of which would be the energy of diffusion. R is a gas constant. At the maximum temperature we have,

$$k_m = c.e^{-E/RT_{max}} \tag{7}$$

where k_m is the value of k at the maximum temperature. Combining equation (6) and (7), we have,

$$k = k_m \cdot e^{-E/RT\left[\frac{T_{max.}-T}{T_{max.}\times T}\right]} \tag{8}$$

where T is any temperatue. If we consider the heat balance at the boundary, the heat produced due to chemical reaction would be balanced by the amount of heat conducted away. Normally speaking, $\triangle H$, the heat produced due to chemical reaction would be constant and hence,

$$\triangle H = K.A.\frac{T_{max.}-T}{\xi} \tag{9}$$

where K is the thermal conductivity co-efficient. We may, therefore, put,

$$T_{max}-T\ \alpha\ \xi = p \tag{10}$$

Accordingly we can write equation (8) in the following form.

$$k = k_m.\ e^{-p\xi} \tag{11}$$

where p is a proportionality constant. Substituating the value of k in equation (5) we have,

$$\xi^2 = 2\ k_m.\ t.\ \exp.\ (-p\xi) \tag{12}$$

Equation (12) is due to Jander[2]. Rigorously speaking equation (12) is not correct and we would simply use equation (12) as an empirical relation.

We shall examine below to what extent equation (12) is satisfied by the data. In figures (3) and (4) log ξ^2/t is plotted against ξ. Straight lines are obtained which confirm equation (12). The behaviour is similar to that reported elsewhere.

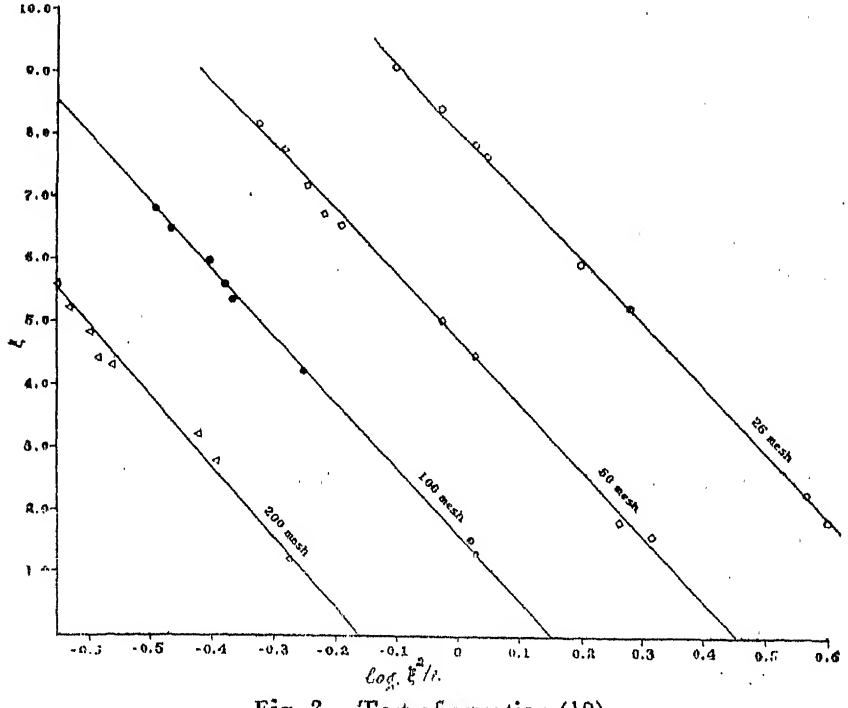

Fig. 3. Test of equation (12).

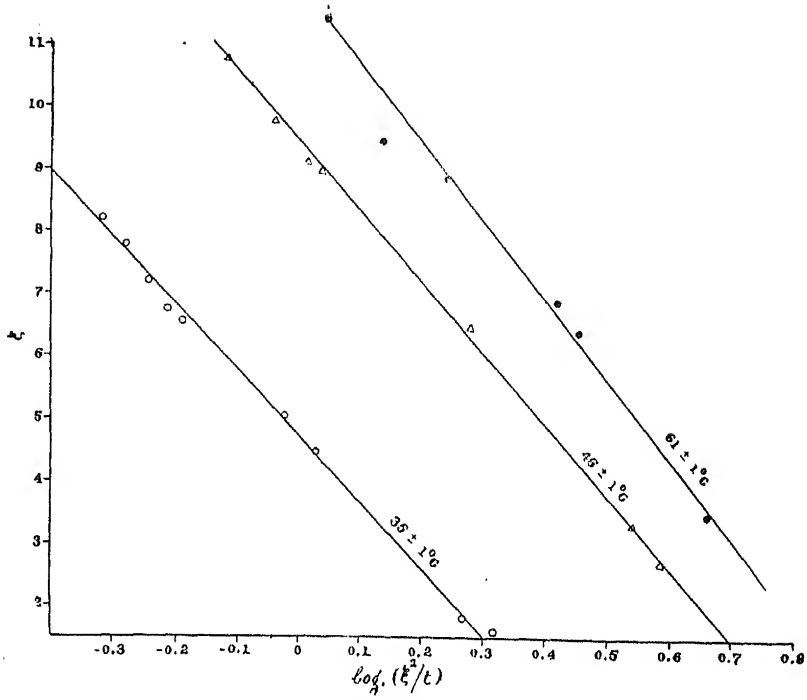

Fig. 4. Test of equation (12).

The values of k_m and p estimated from Figures (3) and (4) are given in Table III.

TABLE III

Parameters if equation (12) at 35± 1°C for different meshes.

Particle size	k_m	p
25 mesh/sq. inch	3·035	0·22
50 mesh/sq. inch	1·44	0·224
100 mesh/sq. inch	0·75	0·2166
200 mesh/sq. inch	0·415	0·2206

TABLE IV

Values of k_m and P for 50 mesh/sq. inch at different temperatures.

Temperature	k_m	p
35± 1°C	1·44	0·224
45± 1°C	3·27	0·1995
61± 1°C	5·89	0·202

It is clear from Tables III and IV that p is sensibly independent of temperature and particle size. k_m depends on particle size and temperature. The activation energy can be calculated from the above data. It is found to be 11·36 Kcal. The value of frequency factor is $1{\cdot}86 \times 10^8$.

5. MECHANISM OF THE REACTION

The over-all kinetic data shows that the reaction is diffusion-controlled. Since naphthalene has appreciable vapour pressure one may suspect that the initial spaces are filled with the vapour which subsequently reacts with picric acid. One may try to find a justification for this in the fact that naphthalene diffuses through the product layer whereas picric acid does not. However, if the reaction takes place through vapour phase as postulated above, the interstices through which vapour can move should be seats of reaction. This is not found to be so. On the other hand the progress of the product layer takes place in a systematic manner governed by equation (12). Whether or not the reaction takes place via solid phase or vapour phase, some mechanism of diffusion of naphthalene molecules through the product layer has to be postulated.

In the above context the dependence of reaction rate on particle size assumes special importance. Normally one would expect that the reaction rate would be increased with decrease in particle size. The experimental data clearly shows that reverse is the case for naphthalene. Smaller particle size means greater surface area but at the same time lesser interstitial space. Since the reaction rate is greater the greater the particle size, the logical conclusion seames to be that at some stage of the reaction, diffusion through interstices is significant.

The most intriguing question is how the reaction is further propogated once the product layer is formed on crystal grain. Several mechanisms have been proposed during recent years. Diffusion may take place through lattice defects.

The activation energy for the reaction under consideration is of the order of 11·36 k cal. If the diffusion of naphthalene is controlled by diffusion in the vapour phase, the energy of activation should be of the order of the heat of sublimation. Since the heat of sublimation of naphthalene is of the order of 14·0 kcal, it would appear that the diffusion through the vapour phase governs the course of reaction. However, for coming to any definite conclusion more careful study of the effect of the particle size and temperature is essential. It would also be interesting to study the corresponding reaction with anthracene, phenanthrene and other hydrocarbons of this series. Such studies are in hand.

The present investigation forms part of the programme of C. S. I. R. Research Unit.

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COLLISION PROCESSES INVOLVING PHONON AND MAGNON*

By

K. P. SINHA *and* U. N. UPADHYAYA

National Chemical Laboratory, Poona-8

ABSTRACT

A theory of the 'Collision Processes Involving phonon-magnon' is developed from the first principles. The crystal field oscillations are treated as perturbations which superpose some excited orbital states on the ground orbital state of the magnetic ion. When use is made of these perturbed states as the starting one electron functions in the second quantization representation, the formulation of the Heisenberg type exchange interaction furnishes the relevant phonon-magnon interaction terms.

Following the above interactions, the phonon magnon relaxation times are calculated for the processes involving one phonon direct process.

Estimates made for iron where the excited, orbitals are taken to be the $4p$ and the ground $3d\gamma$ orbitals, yield values for the relaxation time for the one phonon processes ($T_{sq} \approx 10^{-6}$ sec. at $10^{\circ}k$) in agreement with the suggested results.

INTRODUCTION

The interaction between magnons[1] and phonons is known to play an important role in the relaxation processes occurring in magnetic crystals, particularly at low temperatures.[2]

The first theoretical study was made by Akhiezer[3] from microscopic point of view by expanding the exchange and dipolar terms in power series with normal coordinates of the lattice vibrations. Polder[4], however, has pointed out some difficulties in his calculations.

The recent studies of this problem are based on a phenomenological approach emanating from the macroscopic concepts of the exchange energy density and magnetoelastic coupling energy[5,6,7,8]. Using this method Kittel and Abraham[5], Kaganov and Tsukernik[7] have calculated the time for establishment of equilibrium between the phonon and magnon systems. In as such as the phenomenological approach does not provide a clear insight of the various microscopic processes involved, it is desirable to study the interaction on an atomic model from first principles.

In what follows, we consider the phonon-magnon interaction on an atomic model taking into account the mixing of excited and ground state atomic orbitals owing to crystal field oscillations. This procedure when taken in conjuction with the two electron operator furnishes the relevant interaction Hamiltonian. We then calculate the relaxation times for the establishment of equilibrium between the spin and lattice systems arising through the direct process involving phonons.

2. FORMULATION OF THE INTERACTION HAMILTONIAN

We choose a model consisting of magnetic atoms or ions, regularly arranged as in a crystal, each having in addition to closed shell ion core one localized

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* Communication No. 661 from the National Chemical Laboratory, Poona-8.

electron. The effect of conduction electrons is unimportant as far as phonon-magnon interaction is concerned.[2] The total Hamiltonian consists of the following parts.

$$H = H_e + H_1 + H_c + H_z \tag{2.1}$$

where H_e is the Hamiltonian involving one electron coordinates, namely,

$$H_e = \sum_i \frac{p_i^2}{2m} + \sum_{i,n} U(r_i - R_n) \tag{2.2}$$

H_L = is the lattice Hamiltonian expressed as

$$H_L = \sum_{qp} \hbar\omega_{qp} (b^+_{qp} b_{qp} + \tfrac{1}{2}) \tag{2.3}$$

with b^+_{qp}, b_{qp} standing for the phonon creation and annihilation operators pertaining to wave vector q and branch p^0 and H_c is the electron-electron coulomb interaction operator with the explicit form

$$H_c = \sum_{i \neq j} \tfrac{1}{2} \cdot \frac{e^2}{r_{ij}} = \tfrac{1}{2} \sum_{i \neq j} g_{ij} \tag{2.4}$$

and H_z is the Zeeman term.

In the above $p_i^2/2m$ is the kinetic energy operator of the ith electron, $U(r_i - R_n)$ is its potential energy at r_i due to the ion core at R_n, ω_{qp} is the mode branch frequency of lattice vibration, r_{ij}, the distance between electrons i and j. For the present, the spin-orbit interaction, anharmonic terms in lattice vibrations and dipolar interaction between magnetic ions are not included. For the ith electron the Hamiltonian (2.2) is rewritten as

$$H_e^{(i)} = \frac{p_i^2}{2m} + U(r^i - R_l^\circ) + V_\circ + H' \tag{2.5}$$

$$H' = \sum_h \left(\frac{\partial V}{\partial R_h} \right)_\circ \delta R_h + \tfrac{1}{2} \sum_{h,h'} \left(\frac{\partial^2 V}{\partial R_h \partial R_{h'}} \right)_\circ \delta R_h \, \delta R_{h'} + \quad \ldots (2.6)$$

$$V_\circ = \sum_{m \neq l} U(r^i - R_m^\circ); \qquad R_h = R - R_m$$

Here $U(r_i - R_l^\circ)$ represents the potential acting on the electron when the ion-cores are in undisplaced positions. V_0 is the static crystal field potential due to the nearest neighbour ions acting on the electron i when it is localized at the ion at R_l°. H' represents the first and higher order terms of the Taylor series develop-

ment of the crystal field potential V due to the neighboring ions in the relative displacements of the nearest neighbor ions. We take the wave function $\phi_{a\sigma}$ as the solution of

$$\left(\frac{p^2}{2m} + U(r - \overset{\circ}{R_l}) + V_o\right) \phi_{a\sigma} = E_{a\sigma}\, \phi_{a\sigma} \tag{2.7}$$

The solution of (2.5) which idcludes H′ as the perturbation and mixes some excited states with the ground state functions is represented by

$$\psi_{a\sigma} = \phi_{a\sigma} + \sum_{\alpha} \frac{H'_{\alpha i}\, \phi_{\alpha\sigma}}{E_\alpha - E_a} \tag{2.8}$$

where α represents the excited orbitals, the index σ stands for the spin state. With the above definition of one electron functions, we can write the total. Hamiltonian in occupation number representation by the method of second quantisation as[10],

$$H = H_L + \sum_{a\sigma} E'_{a\sigma}\, A^+_{a\sigma} A_{a\sigma} + \tfrac{1}{2} \sum_{\substack{a,b,c,d \\ \sigma\sigma'}} A^+_{a\sigma} A^+_{b\sigma'} < a\sigma, b\sigma' \mid g_{12} \mid c\sigma, d\sigma' > \times A_{c\sigma}\, A_{d\sigma'} + H_z \tag{2.9}$$

where $A_{a\sigma}{}^+$, $A_{a\sigma}$ represent the creation and annihilation operators respectively for the one electron states $\psi_{a\sigma}$ and obey the following relation :

$$\left.\begin{aligned} A_i\, A_k{}^+ + A_k{}^+\, A_i &= \delta_{ik} \\ A_i\, A_k + A_k\, A_i &= 0 \\ A_i{}^+ A_i &= N \end{aligned}\right\} \tag{2.10}$$

where k is the common index for both orbital and spin states, and N_i the occupation number of the state i. Now, as the operators $A_i{}^+$, A_i and N_i are related to to the conventional spin operators of the electron, we can write the part of the total Hamiltonian consisting of $H_e + H_c + H_z$ in terms of the spin operators. Further, using the H. P.[11] spin deviation and other operators, defined as:

$$\begin{aligned} S^l &= (2S)^{\frac{1}{2}} \left(1 - \frac{a_l{}^+ a_l}{2S}\right)^{\frac{1}{2}} \\ S^1_- &= (2S)^{\frac{1}{2}} a_l{}^+ \left(1 - \frac{a_l{}^+ a_l}{2S}\right)^{\frac{1}{2}} \\ S - S^l_z &= a_l{}^+ a_l = n_e \text{ (the spin deviation).} \end{aligned} \tag{2.11}$$

and their Fourier transforms given as

$$a_\lambda = \frac{1}{\sqrt{N}} \sum_l \exp(ik_\lambda \cdot R_l^0)\, a_l$$

$$a_\lambda^+ = \frac{1}{\sqrt{N}} \sum_l \exp(-ik_\lambda \cdot R_l^0)\, a_l^+$$

$$a_l = \frac{1}{\sqrt{N}} \sum_\lambda \exp(-ik_\lambda \cdot R_l^0)\, a_\lambda$$

$$a_l^+ = \frac{1}{\sqrt{N}} \sum_\lambda \exp(ik_\lambda \cdot R_l^0)\, a_\lambda^+ \qquad (2.12)$$

where k is the reduced wave vector for magnons, we can express the phonon-magnon interaction terms contained in the Hamiltonian (2.9) as:

$$H_{(int)} = \frac{4}{\sqrt{N}} \sum_{h\lambda qp} 2S\, {}^{\alpha}J(R_h) \left[e^{ik_\lambda \cdot R_h} - e^{i(k_\lambda - q) \cdot R_h} + e^{-iq \cdot R_h} - 1 \right] \times g_{qp}\, a_\lambda^+ - q\, a_\lambda\, (b_{qp}^+ - b_{-qp}) \qquad (2.13)$$

+ (higher order terms in phonon operators)

Here,

$${}^{\alpha}J(R_h) \equiv \sum_\alpha \frac{\langle \phi_\alpha^{(1)}\ \phi_m^{(2)} \mid g_{12} \mid \phi_m^{(1)}\ \phi_l^{(2)} \rangle \langle \phi_\alpha \mid V^h \mid \phi_l \rangle}{(E_\alpha - E_l)}$$

$$V^h = \left(\frac{\partial V}{\partial R_h} \right)_0 \qquad (2.14)$$

The following momentum conservation relation holds between the phonon and magnon wave vectors for the direct process involving phonons considered here and have already been ultilized in deriving (2.13)

$$k_\lambda' + q - k_\lambda = 0 \qquad (2.15)$$

3. EQUILIBRATION BETWEEN HAGNONS AND PHONONS

We calculate the transition probabilities of the various processes connecting the initial and final states using the well known time dependent perturbation expression

$$W_{if} = \left(\frac{2\pi}{\hbar} \right) \mid H_p \mid^2_{if} \delta(E_i - E_f) \qquad (3.1)$$

Using (3.1) and (2.13) the transfer of energy between the magnon and phonon systems is expressed as:

$$\dot{Q} = \sum_{qp} \hbar\omega_{qp} < \dot{N}_{qp} >$$

$$= \frac{2\pi}{\hbar} \sum_{qp\lambda} | \Phi_{\lambda qp} |^2 \hbar\omega_{qp}$$

$$\times \left\{ (n_{\lambda-q}+1)(n_\lambda)(N_{qp}+1) - (n_{\lambda-q})(n_\lambda+1)(N_{qp}) \right\}$$

$$\delta(E_{\lambda-q}+E_{qp}-E_\lambda). \qquad (3,2)$$

where

$$\Phi_{\lambda qp} = \frac{4}{\sqrt{N}} \sum_h 2S\ {}^{\alpha}J(R_h)\left[e^{ik_\lambda \cdot R_h} - e^{i(k_\lambda - q)\cdot R_h} - 1 + e^{-iq\cdot R_h} \right] g_{qp} \qquad (3.3)$$

Let T_s and T_l be the spin and lattice Temperatures respectively which govern the equilibrium Bose distribution of magnons and phonons. Thus with $T_s = T$ and $\Delta T = T_s - T_l$, we can write (3.2) after developing the terms containing $(T - \Delta T)$ in terms of Taylor series in powers of ΔT. Keeping only first order terms, we get:

$$\dot{Q} = \frac{2\pi}{\hbar} \frac{\Delta T}{T^2} \sum_{qp\lambda} | \Phi_{\lambda qp} |^2 \frac{(\hbar\omega_{qp})^2}{k}$$

$$\times \frac{e^{E_\lambda / kT}}{\left(e^{E_{\lambda-q}/kT}-1\right)\left(e^{E_\lambda/kT}-1\right)\left(e^{E_{qp}/kT}-1\right)} \delta(E_{\lambda-q}+E_{qp}-E_\lambda) \qquad (3.4)$$

Now, it is very difficult to evaluate $\dot{Q}$ in general case, so we follow closely the method suggested earlier[3], and find out the values for the limiting cases of low and high temperatures.

Low Temperature Limit: $(\beta >> 1)$

$$\dot{Q} = \frac{2^9 . 3N}{\pi^3} \left(\frac{\hbar}{Mk}\right) \frac{\Delta T}{T^2} \frac{T^6}{\theta_D^2 \theta_c^4} \exp\left[-\frac{\beta}{4}\right] \left[{}^{\alpha}J(R_h)\right]^2 S^2 \qquad (3.5)$$

where $\theta_c = 2JS/k$, $\theta_D = \hbar vs/ka$; $\beta = \dfrac{\theta_D^2}{\theta_c T}$

The exponential decrease of energy transfer with decreasing temperature in (3.5) is the same as that obtained by Akhiezer and others, however, there are important differences in other factors.

High Temperature Limit: $(\beta \rightarrow 0)$

In this case, neglecting in the final expression for $\dot{Q}$ terms in (θ_D/T) higher than two get

$$\dot{Q} = \frac{2N}{3\pi} \left(\frac{\hbar}{Mk} \right) \frac{\Delta T}{T^2} \left(\frac{T\,\theta_D}{\theta_c} \right)^2 S^2 \left[{}^{\alpha}J(R_h^{\circ}) \right]^2 \tag{3.6}$$

It may be noted that $\dot{Q}$ in the higher temperature limit becomes independent of temperature in our mechanism.

4. RELAXATION TIME FOR EQUILIBRATION

We now proceed to calculate the relaxation times for the establishment of equilibrium between the magnon and phonon systems owing to the one phonon process discussed in the proceeding section. The relevant expression is given by[5]

$$\frac{1}{\tau_{sp}} = \frac{\dot{Q}\left(\frac{1}{C_S} + \frac{1}{C_L} \right)}{\Delta T} \tag{4.1}$$

where τ_{sp} is the relaxation times, C_s and C_l the specific heats of the spin and lattice systems. The following explicit forms for these are taken, for low temperature limits, [3,12]

$$C_{sp} = \frac{15}{32} \frac{1}{\pi^{3/2}} kN \left(\frac{T}{\theta_c} \right)^{3/2}; \; C_l = \frac{12\pi^4}{5} kN \left(\frac{T}{\theta_D} \right)^3 \tag{4.2}$$

Using the expression for $\dot{Q}$ in the preceding section, the relaxation time for the low and high temperature limits are given by:

(*i*) *Low temperature limit*: $(\beta >> 1)$

$$\frac{1}{\tau_{sp}} = \frac{3 \times 2^9}{\pi^3} \left(\frac{\hbar}{Mk^4} \right) \frac{T^4}{\theta_D{}^2 \theta_c{}^4} \left(\frac{\theta_c}{T} \right)^{3/2} \left(11 + \frac{\beta^{3/2}}{234} \right)$$

$$\times \exp\left[-\frac{\beta}{4} \right] S^2 \left[{}^{\alpha}J(R_h^{\circ}) \right]^2. \tag{4.3}$$

(ii) *High temperature limit:*

In the high temperature limit, the specific heat of the lattice reduces to the well known expression $3Nk$. For the spin system, however, analogous expression has not been suggested so far. The expression for C_s given in (4.2) is valid only at low temperature. As in the case of crystallattice vibration, if we take the upper limit of magnon wave vectors as $1/a$, then for the high temperature limit one arrives at the expressson for the specific heat of the spin system as $C_s \sim Nk/6\pi^2$ which is much smaller than the lattice specific heat at high temperatures. It is interesting to note that the characteristic temperature for the spin system implicit in the above assumption is the same as the temperature θ_c . Thus (4.1) becomes, neglecting $1/C_l$

$$\frac{1}{\tau_{sp}} \approx 4 \left(\frac{\hbar}{Mk^2}\right) \left(\frac{\theta_D{}^2}{\theta_c{}^4}\right) s^2 \left[{}^{\alpha}J(R_h) \right]^2 \qquad (4.4).$$

which is independent of temperature. This point has not been noted before; however, one must bear in mind that the spin wave approximation breaks down at high temperature regions and there may not be any physical significance in calculations pertaining to high temperature limits.

5. ESTIMATES AND DISCUSSION

In the expressions for the various relaxation times derived in the previous section, most of the factors are easily determined except those involving ${}^{\alpha}J(R_{ho}{}^{\circ})$. A knowledge of this will require the calculation of the exchange integrals involving excited orbitals as well as the matrix elements of the various derivatives of the crystal field potentials with respect to excited and ground state orbitals. We consider an order of magnitude estimate of these quantities for a body centered cubic systems such as iron. The excited orbitals for iron are taken to be the $4p$ empty orbitals. Thus the transition involved are $3d$ to $4p$, which for the cubic symmetry of the system can be achieved owing to odd vibrations of the surrounding ions with respect to the ion in question. For the actual estimate, we consider a collinear system of three ions lying on the body diagonal of the unit cell and get

$$< \Psi_{3dz^2} \mid V^h \mid \Psi_{4pz} > \sim 1{\cdot}25 \times 10^{-3} \text{ dynes.}$$

The energy denominator $\Delta E_{\alpha} = E_{\alpha} - E_0$ is taken to be the difference in $4p$ and $3d$ bands for iron series metals. This is estimated

from X-ray spectroscopy data[13] as $\Delta E_{\alpha} \approx$ 5ev. A reasonable range will be 5 to 10 e. v., however to be on the safe side we shall use the value $\Delta E_{d-p} \sim$ 10 e. v. For an estimate of the exchange integrals of the type

$$< \psi_{p}^{(1)} \psi_{3d}^{(2)} | g_{12} | \psi_{3d}^{(1)} \psi_{3d}^{(2)} >$$

We make use of the calculations of similar integrals, in certain other magnetic studies.[14,15] The value is of the order of ·01 a. u. (0·27 e. v.). We use the value of 0·1 e. v. in our estimate.

Thus for iron, at T = 10°K,

we get estimate of $(1/\tau_{sp}) \sim 2{\cdot}5 \times 10^{6}$ sec^{-1}

$$i.\,e.\ \tau_{sp} \approx 10^{-6} \text{ sec.}$$

For the one phonon process with S = 1. This estimate seems to be of the right order of magnitude as can be seen by comparing with the values suggested earlier [3,5] For the high temperature limit, we get the value of τ_{sp} as 10^{-11} sec. This value may be taken to be the limiting value since $(1/\tau_{sp})$ in this limit becomes independent of temperature. From this it is reasonable to expect that at room temperature τ_{sp} will be around 10^{-8} to 10^{-9} sec. in agreement with that suggested by Bloembergen and Damon[16].

The estimate of τ_{sp} arising out of two phonon processes, following the above procedure shows that the value at low temperatures are extremely small. Hence, these processes are unimportant compared to one phomon processes discussed above.

Details of the work discussed above has been published elsewhere.[17]

ACKNOWLEDGMENT

We are grateful to Dr. A. B. Biswas for his interest in this work. One of us (U. N. Upadhyaya) is indebted to the Council of Scientific and Industrial Research, New Delhi for the grant of a fellowship which made this study possible.

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ARUN K. DEY

Officer-on-Special Duty

The Thirtythird annual meeting of the Academy was held at the University of Allahabad on February 15 and 16, 1964. The meeting was held mainly to transact official business and no sessions for reading of papers were held. Two Symposia on (*i*) The Chemistry of Natural Products, and (*ii*) Land Fertility, Improvement and Alkali Soil Reclamation by Blue Green Algae, were organized which were attended by a large number of participants.

The delegates to the annual meeting were from all over the country and also included Dr. Miss E. C. M. Segar, a botanist from New Zealand.

The inaugural meeting, which was held on the first day at 2-30 p.m. in the Vizianagram Hall of the University was presided over by Professor P. Maheshwari, President of the Academy. His Presidential Address was on "Science and Government," in which he dealt at length with the conditions under which science fluorishes in India, and the handicaps that have to be faced by scientific workers. He also put forward suggestions to overcome them and pleaded for greater facilities for research work.

Dr. S. Bhagavantam, Scientific Adviser to the Minister for Defence, Government of India, inaugurated the meeting. In his address on "Physics of the Earth", he said that the study of the earth revealed that our planet is only an infinitesimal

part of the universe both in respect of size and time. Man has been trying to know more and more about the earth. With their attempts towards this end they have developed a greater urage to conduct further researches.

The Uttar Pradesh Education Minister's Gold Medal for Botany and Agriculture was awarded to Dr. K. S. Bilgrami, Reader in Botany, University of Jodhpur.

Dr. R. K. Saksena, General Secretary, read the Secretaries' Report and announced the names of the new members of the Council.

The meeting commenced with the singing of Bande Mataram and ended with the National Anthem by the students of Mahila Shilpa Bhavan.

In the evening, a popular lecture on "Symmetry : Its principles and practice" was delivered by Dr. S. Bhagavantam. The Symposia opened in the evening after the popular lecture and continued the next day.

The Scientific Instrument Co. Ltd., Allahabad was 'At Home' to the members and the delegates and the Academy is thankful to the Directors of the company for their courtesy.

The Academy records its thanks to the Vice-Chancellor, University of Allahabad for allowing the use of the premises of the University for the meetings and to the Principal, Mahila Shilpa Bhavan for their cooperation in arranging the opening and the closing songs at the inaugural meeting. The Academy also appreciates the cooperation of the members, the participants and all others, who contributed to the success of the annual meeting.

PROGRAMME

SATURDAY, The 15th February, 1964

2·30 P. M. Annual Meeting (*Physics Lecture Theatre*).

1. Bande Mataram by the girl students of Mahila Shilpa Bhavan.
2. Appointment of two scrutineers by the President to count votes.
3. Annual Report by Dr. R. K. Saksena, General Secretary.
4. Inaugural Address : "Physics of the Earth" by Dr. S. Bhagavantam.
5. Presidential Address : "Science and Government" by Prof. P. Maheshwari.
6. Presentation of the Uttar Pradesh Government Education Minister's Gold Medal.
7. Announcement of Office Bearers for 1964 by the General Secretary.
8. Votes of thanks.
9. National Anthem.

4·15 P. M. Group Photograph of Members of the Academy, Delegates and participants in the Symposia (*Physics Department*).

4·30 P. M. "At Home" by the courtesy of the Scientific Instrument Co. Ltd., Allahabad (*M. C. C. Quadrangle*).

5·00 P. M. Popular Lecture : Symmetry, its principles and Practice" by Dr. S. Bhagavantam (*Physics Lecture Theatre*).

6·00 P. M. Symposium on the Chemistry of Natural Products (*Chemistry Lecture Theatre*).

7·00 P. M. Symposium on Land Fertility, Improvement and Alkali Land Reclamation by Blue Green Algae (*Chemistry Lecture Theatre*).

SUNDAY, The 16th February, 1964

9.30 P. M. (i) Symposium on the Chemistry of Natural Products (*Chemistry Lecture Theatre*).

(ii) Symposium on Land Fertility, Improvement and Alkali Land Reclamation by Blue Green Algae (*Botany Lecture Theatre*).

2·00 P. M. Symposia (continued).

4·00 P. M. At Home (*Lawn of the Botany Department*).

5·00 P. M. Symposia (Concluding session).

THIRTY-THIRD ANNUAL MEETING

ALLAHABAD, February 15 & 16, 1964

Group Photograph of Delegates and Members

From Left to Right

Sitting on Chairs—Prof. S. N. Ghosh, Prof. N. R. Dhar, Prof. A. C Banerji, Dr. B. N. Prasad, Prof. P. Maheshwari, Dr. S. Bhagavantam, Dr. Balbhadra Prasad, Dr. R. K. Saksena, Prof. M. D. L. Srivastava, Prof. R. N. Tandon, Dr. Miss E. C. M. Segar.

Standing 1st Row—Prof. U. N. Chatterji, Dr. S. G. Misra, Dr. K. D. Vyas, Dr. G. Panigrahi, Shri G D. Srivastava, Dr. S C Gupta, Dr. Amar Singh, Dr. K. S. Bilgrami, Dr. A. K. Mitra, Dr. S. P. Tandon, Shri V. B. Shankaram, Dr. R. Sahai, Dr. A. L. Jagannadha Rao, Shri M. Swaleh, Dr. K. Majumdar.

Standing 2nd Row—Dr. B S. Mehrotra, Dr. L. N. Johri. Dr. G. S. Sidhu, Shri T. J. Varkey, Dr. N. S Narashimhan, Dr. S. C. Prakashi, Dr. S. C. Sen Gupta, Dr. Sudhir Chandra, Dr. Ram Kumar, Shri I. C. Shukla, Dr. Niranjan Das, Shri L. M. Tripathi, Dr. S. S. Deshpande, Dr J. D. Tewari, Dr. Mrs. R. Pant.

Standing 3rd Row—Miss T. Joshi. Dr. B. B. L. Saxena, Shri K. C. Nand, Shri J. P. Ambasht, Shri S. K. Gaur, Dr. G S. Misra, Shri S. N. Srivastava, Prof. O. N. Perti, Dr. S. K. De, Dr. J. B. Lal, Shri H. P. Srivastava, Shri P. D. Satsangi, Dr. P. C. Gupta, Miss S. Agrawal.

Standing 4th Row—Shri B. Lal, Shri N. Ram, Shri B. S. Rao, Dr. J. P. Sharma, Dr. V. N. Sharma, Dr. S. P. Srivastava, Shri J. Prasad, Dr. S. N. Bhargava, Dr. A. K. Dey, Dr. S. P. Mushran, Dr. R. D. Tiwari.

12. Shri Hemraj Kothari, B.Sc., D.W.P. A.C.C.G.I., A.M.S.E., F.C.I., F.B.I.S., Management and Technical Consultant and Chief Executive, Kothari Consultants, 12-India Exchange Place, Calcutta-1.

13. Shri K. C. Gupta, M.Sc., Lecturer in Mathematics, University of Rajasthan, Jaipur.

14. Shri S. C. Verma, M.Sc., Lecturer in Botany, Panjab University, Chandigarh.

15. Dr. S. H. Rasul, M.Sc., Ph.D., Reader in Geology, Aligarh Muslim University, Aligarh.

16. Prof. T. A. Davis, B.A., P.G. Dip. (Crop Botany), Professor of Crop Science, Indian Statistical Institute, Calcutta.

17. Dr. Y. R. Tripathi, D.Sc., Deputy Director of Fisheries, Dept. of Animal Husbandry and Fisheries, Badshah Bagh, Lucknow.

18. Prof. P. R. Khandekar, M.A., Professor of Mathematics, M. V. Mahavidyalaya, Bhopal.

19. Dr. Md. Mahfooz Ali Siddiqui, M.A., Ph.D., Lecturer in Mathematics, Osmania University, Hyderabad-7.

20. Shri L. M. Tripathi, M.A., Research Scholar in Mathematics, Allahabad University, Allahabad.

21. Shri P. K. Sundararajan, B.A. (Hons.), Lecturer in Mathematics, St. Francis de Sales College, Seminary Hills, Nagpur.

22. Dr. (Mrs.) Gyan Vati, D.Phil., Junior Scientific Officer, Defence Research Laboratory (Stores), Kanpur.

23. Dr. K. N. Srivastava, M.Sc., D.Phil., Lecturer in Mathematics, M.A. College of Technology, Bhopal.

24. Dr. T. A. Hariharan, M.Sc., Ph.D., Lecturer in Physics, Karnataka Regional Engineering College, Suratkal. S. K. (Mysore State).

25. Dr. Rama Shanker Rai, M.Sc., D.Phil., Post-Doctoral Research Associate (A.E.C.), Radiochemistry Laboratory, Chemistry Department, Washington University, St. Louis-30, Mo. (U.S.A.)

FELLOWS

We have pleasure to announce the elecion of the folowing new Fellows of the Academy during the year 1963.

1. Dr. S. K. Banerji, M.Sc., D. Phil., Head, Chemistry Department, Birla College of Engineering, Pilani (Rajasthan).

2. Dr. K. S. Bilgrami, M.Sc., D.Phil., D.Sc., Reader in Botany, University of Jodhpur, Jodhpur.

3. Prof. R. S. Kushwaha, M.Sc., D.Phil., Ph.D., Head, Mathematics Dept., University of Jodhpur, Jodhpur.

4. Dr. Y. Satyanarayana, B.Sc., Ph.D., Ecologist, Central Arid Zone Research Institute, Jodhpur.

MEETINGS

During the year under review, nine meetings of the Council, six meetings of the General Body and two meetings of the Fellows were held. Besides the transaction of business, papers were read and discussed at the ordinary meetings.

THIRTY-SECOND ANNUAL MEETING

The thirty-second annual session, which was to be held at Chandigarh on the invitation of the Panjab University, had to be cancelled due to national emergency, and the annual meeting, mainly to transact essential business according to the rules of the Academy, was held on Saturday, the 16th February 1963 in the Vizianagram Hall of the University of Allahabad.

The meeting was inaugurated by Dr. D. S. Kothari, M.Sc., Ph.D. (Cantab.), F.N.I., Chairman, University Grants Commission, New Delhi, who delivered his address on "Science and Human Progress". In the absence of Prof. S. Ghosh, President of the Academy, Dr. B. N. Prasad was in the chair.

The meeting terminated with a popular lecture on "Elementary Particles" by Dr. Kothari.

The academy records its thanks to the Vice-Chancellor of the University of Allahabad for kindly allowing the use of the premises of the University for the meeting and for an "At Home" to the participants.

COUNCIL

The following constituted the Council of the Academy during 1963.

President

Prof. P. Maheshwari, D.Sc., F.N.I., F.B.S., F.A.Sc., F.N.A.Sc., Delhi.

Vice-Presidents

Prof. S. Ghosh, D.Sc., F.N.I., F.N.A.Sc., Jabalpur.

Dr. B. N. Prasad, Ph.D., D.Sc., F.N.I., F.N.A.Sc., Allahabad.

Honorary Treasurer

Prof. R. N. Tandon, M.Sc, Ph.D., D.I.C., F.A.Sc., F.N.A.Sc., Allahabad.

Foreign Secretary

Prof. S. N. Ghosh, D.Sc., F.N.A.Sc., Allahabad.

General Secretaries

Dr. R. K. Saksena, D.Sc., F.N.I., F.N.A.Sc., Allahabad.

Dr. A. G. Jhingran, M.Sc., Ph.D., F.N.I., F.G.M.S., M.M.G.I., F.N A.Sc., Calcutta.

Members

Prof. N. R. Dhar, D.Sc., F.R.I.C., F.N.I., F.N.A.Sc., Allahabad.

Dr. A. C. Joshi, D.Sc., F.N.I., F.N.A.Sc., Chandigarh.

Dr. S. Ranjan, D.Sc., F.N.I., F.A.Sc., F.N.A.Sc., Allahabad.

Prof. A. C. Banerji, M.A., M.Sc., F.R.A.S., F.N.I., F.N.A.Sc., I.E.S. (Retd.), Allahabad.

Col. Dr. P. L. Srivastava, M.A., D.Phil., F.N.I., F.N.A.Sc., Muzaffarpur.

Dr. S. H. Zaheer, M.A., Dr.Phil.Nat., F.N.A.Sc., New Delhi.

Prof. M. D. L. Srivastava, D.Sc., F.N.A.Sc., Allahabad.

Prof. Raj Nath, Ph.D., D.I.C., F.N.I., F.N.A.Sc., Varanasi.

Prof. D. S. Srivastava, M.Sc., Ph.D., F.R.M.S., F.R.E.S., F.N.A.Sc., Sagar.

REPRESENTATIONS ON OTHER ORGANISATIONS

The Academy was represented by the following members on other organisations and learned bodies :—

1. Prof. N. R. Dhar, D.Sc. (London & Paris), F.N.I., I.E.S., (Retd.), Additional Vice-President, National Institute of Sciences of India.
2. Dr. R. K. Saksena, D.Sc., (Paris), F.N.I., Additional Member, Council of National Institute of Sciences of India.
3. Prof. N. R. Dhar, D.Sc., (London & Paris), F.N.I., I.E.S, (Retd.), Member of the Indian National Commission for Cooperation with UNESCO.
4. Dr. R. K. Saksena, D.Sc. (Paris), F.N.I., A representative of the Academy on the Court of the Lucknow University.

FINANCES

The financial position of the Academy is given in the Financial Statement for 1962-63 ending on the 31st March, 1963.

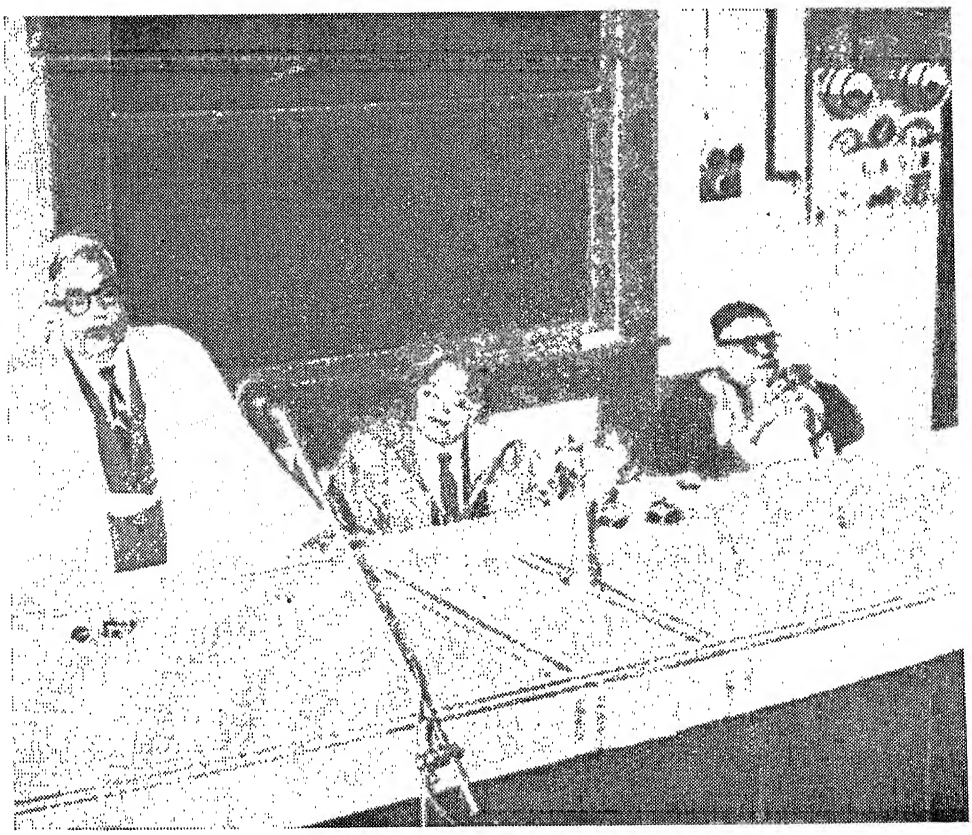
The Academy is thankful to :

1. The Government of India,
2. The Government of Uttar Pradesh,
3. The University of Allahabad,

and 4. The National Institute of Sciences of India, New Delhi, for the assistance received from them.

The Academy continues to work under great financial difficulties. The office, publication and library are being reorganized and we require more office, technical and administrative staff for them.

Dr. R. K. Saksena reading the Secretaries' Report.



A view of the dais.

FINANCIAL STATEMENT FOR THE YEAR 1962-63

INCOME

		Rs.
Opening Balance (1-4-62)	...	1,581.89
U. P. Govt. recurring grant for 1962-63	...	6,000.00
Govt. of India Non-recurring grant for 1962-63	...	10,000.00
Allahabad University Grant for 1962-63	...	1,000.00
Membership Subscription	...	3,405.25
Life Membership Subscription	...	3,021.39
		+ $ 27.00
Sale of Proceedings	...	10,067.25
Cost of Reprints	...	394.18
Bank Commission	...	17.47
Transfer from Reserve Fund	...	8,000.00
Provident Fund contribution from the staff	...	290.62
Loan realised	...	66.00
Amount of refund (Annual Session)	..	107.58
Excess amount deposited in the bank against Bill No. 70, dated 24-12-60	...	21.45
Interest on fixed deposit (Life Membership)	...	.56
Fine realised	...	14.00
Total	...	43,987.64
		+ $ 27.00

EXPENDITURE

			Rs.
Recurring:			
Establishment		...	6,049.22
Dearness Allowance		...	1,568.36
Provident Fund		...	581.24
Postage		...	2,161.73
Printing and Stationery		...	779.94
Annual Session Expenditure		...	2,282.90
Transfer to Reserve Fund		...	11,061.95
(*a*) Refund of the amount taken from Reserve Fund	Rs. 8,000.00		
(*b*) Life Membership Fee	Rs. 3,021.39		
(*c*) Refund of the amount received from Dr. H. S. Choudhuri, Gorakhpur	Rs. 40.00		
(*d*) Interest on fixed deposit	Rs. .56		
Cost of publication of Journal		...	15,024.47
(*a*) Mission Press	Rs. 4,301.85		
(*b*) Capital Press	Rs. 5,768.84		
(*c*) Cost of Printing paper	Rs. 4,306.53		
(*d*) Cost of Real Art paper	Rs. 294.78		
(*e*) Cost of other paper	352.47		
Total Recurring Expenditure		...	39,509.81
Non-recurring:			
(*a*) Bank charges and devaluation of dollars	Rs.		86.52
(*b*) Loan advanced to Sri Sakhan Lal	Rs.		100.00
(*c*) Repairs of Building	Rs.		194.03
(*d*) Cost of bicycle	Rs.		196.60
(*e*) Subscription account	Rs.		100.00
(*f*) Adjustment of amount wrongly credited by the State Bank of India	Rs.		64.98
(*g*) Refund of the subscription paid by M/s. Peoples Publishing House, New Delhi	Rs.		56.88
(*h*) Audit Fee	Rs.		200.00
(*i*) Contingent Expenses	Rs.		1178.83
Total of Non-recurring Expenditure	Rs.		2177.84
Grand Total of Expenditure	Rs.		41,687.65
Cash in hand (31-3-63)	Rs.		14.09
Bank balance	Rs.		2,285.90
			+ $ 27.00
Total		...	43,987.64
			+ $ 27.00

Presidential Address

SCIENCE AND GOVERNMENT

By

Professor P. MAHESHWARI, D.Sc., F.N.I., F.B.S., F.A.Sc., F.N A.Sc.

Head of the Botany Department, University of Delhi, Delhi

MEMBERS OF THE ACADEMY, LADIES AND GENTLEMEN!

I consider it a great honour and a privilege to be elected President of the National Academy of Sciences. It is an additional pleasure for me that this meeting of the Academy is being held at Allahabad which has long been a famous seat of learning. It is here that I started my college career 43 years ago under the guidance of a great missionary, the late Dr Winfield Dudgeon, and for a period of two years I also served as a Lecturer in the botany department of the Allahabad University. I am happy to note that among the audience today there are some under whom I had the privilege of studying for my B.Sc. and M.Sc. degrees, others who were my classfellows or colleagues, and still others whom I like to think of as old pupils. I always consider Allahabad to be my first home and therefore my pleasure is by no means inconsiderable in being with the elite of the town this afternoon.

I gave long thought to the topic of my address to you today. It would have been easy enough to speak about the work that I have been doing recently at Delhi but with the present trends in specialization and the fact that only a small fraction of the audience would be engaged in botanical research, I tried to think of a broader and different field and finally decided to talk to you today about the conditions under which science flourishes, what are our shortcomings in this respect, and how we can overcome them.

THE SCIENTIFIC REVOLUTION

We are living in the midst of the most explosive scientific revolution the world has ever seen. On the one hand we are looking into the secrets of life itself and are apparently on the verge of synthesizing it; on the other hand we are penetrating the outer space by means of rockets and sputniks. Whereas the USA retains the general overall lead, in space science the USSR has surpassed all countries. Although we in India do not need to join this race into space, science as such is of the utmost importance to us for improving the health of the people, for providing them with adequate food and shelter and for keeping the population under control. Our industries and our agriculture will not be able to develop except with the support of science. That we have made a little progress in the last decade is no ground for complacency, for meanwhile our population has been increasing at the rate of 2 per cent per annum. In fact the gap between hunger and self-sufficiency remains unbridged and the condition of the ordinary man is only slightly better

than before. To prosper in peace, to resist the invader, and to command the respect of our neighbours we need one thing above all and that is science.

If the challenge is to be met soundly and squarely, we must have a great deal more of science—both in quality and quantity—than we have had so far. There are also some areas of science which impinge to a greater extent upon our life than others and these will have to be tackled specially.

Although nations and governments do not make scientific discoveries (these are made by individuals), in the present world the scientist and the government have a close relation to each other. The days are long past when solitary individuals with a few small pieces of equipment and sheets of paper could sit in a corner or in a garden and carry on their observations and calculations. That was the way Archimedes, Newton, Galileo, Harvey, Vesalius and Mendel worked. However, modern science has advanced at an incredibly fast rate. Presently, scientists have to be trained on a vast scale; they have to be fostered with great care and consideration; they have to be given laboratories with complicated fittings and costly equipment (cyclotrons, biotrons, seismographs, computors, oceanographic ships, etc.); and provided with a whole staff of collaborators, technicians and assistants. This requires money at a scale which was unthinkable even 10 years ago. Here comes the role of the government. It is the government alone which can supply the buildings, men and money, and sustain research workers on an ever increasing scale.

THE EDUCATIONAL BACKGROUND

There was a good deal of excellent science in ancient India and in some ways we even led the rest of the world, but this lead was unfortunately not kept up and we got into slumber. There was an awakening in the 19th and 20th centuries and we produced some excellent scientists like Ramanujam, J. C. Bose, P. C. Ray, M. N. Saha, B. Sahni, K. S. Krishnan (among those who are living the name of C.V. Raman is pre-eminent) but for a large country with such a huge population, this is insignificant. Since no nation has a monopoly on intelligence and our genetic potential is in no way inferior to that of the wealthier and more advanced nations, the trouble naturally lies elsewhere. How to improve the situation so as to get the best out of our scholars and what should be done in order to increase the number of good scholars are questions that loom large before us. They are indeed the most important questions of the day, although they seldom appear in the newspapers.

In order to increase the number of persons engaged in a scientific career we must naturally start at the school stage. With the increasingly important role that science is destined to play in our lives, it is imperative that no student should pass the Higher Secondary or High School examination without an integrated course in science. It is a pity that even at the school level science is taught in bits like Physics, Chemistry, Mathematics and so on, and many go through their school career without any knowledge of the life sciences at all—without knowing how their bodies work, how food is manufactured by plants, and how it is digested by animals and human beings. This is a sorry state of affairs and needs to be rectified at once.

To attract better students to a science career the Government must emphasize by all possible means, such as popular articles and announcements in the press, that scientists can render a vital service to the country and that suitable positions with adequate salaries would be available to all young men who have undergone a training in science. We must also increase not only the number but also the value

of the scholarships in science. The present scheme for search of talent (launched by the National Council of Education Research and Training) is to be welcomed for here an attempt is being made to test the students for their aptitude in science and to finance their future studies in places which are most suited for this purpose.

In addition, of course, the facilities for the study of science in schools and colleges have to be vastly improved. The nation's scientists may be diagrammed as a sort of pyramid with the students of the Higher Secondary level forming the base. Some of them will be unsuccessful and a good many will drop out for other reasons. This will also recur at the B.Sc. and M.Sc. levels and finally only a small percentage will do successful research for the Ph.D. It is therefore obvious that to obtain a few top leaders in science, there has to be a large base of reasonably good quality from which there will be repeated skimmings of the cream at successively higher levels. At the same time we must reduce the casualties at the various levels not by lowering the standards but by increasing the efficiency of the teachers and our educational system. The best teachers, it has been found, are almost always able to motivate and inspire students to hard work and a thorough study of their subject. By thus giving the opportunities for a scientific career to all who are above the average, we shall build up not only some fine scientists but also create a scientific environment in the whole country. In other words we shall have a populace which will have sympathy for science, which will set some tasks for scientists and which will in turn do something to fulfil the demands of the scientists themselves.

CENTRES OF ADVANCED STUDY

While it is important to improve the science education in our schools and colleges, it is even more essential to raise the quality of the research work of our Ph.D. students and staff. It is naturally not possible to collect all the fine equipment in every science department and for all branches of a subject. The UGC has, therefore, very wisely adopted the policy of establishing several advanced centres of research in favourable places. For this they have provided some extra staff and equipment as well as a grant for recurring expenditure. This, I am sure, is a move in the right direction and it is hoped that additional centres will be started from time to time. The men trained at these centres will be available to other universities to strengthen their departments, and the possibility of receiving these extra grants may well start a spirit of healthy competition between one institution and another. It is of course important to see that this pursuit of excellence is genuine and no other criterion except sheer merit is allowed to influence the decision of the UGC in setting up these centres.

EMPLOYMENT OF WOMEN SCIENTISTS

Although the Indian Constitution guarantees equal rights to both men and women, it is rare to find women scientists in the employment of the Government or the Universities. Due to the limitations imposed by marriage, the scarcity of house-maids, the chores to be performed every day at home, and the emotional strain of raising a family, women are often unable to devote long hours of continuous work. After their college and university education is over, they adopt a rather casual attitude to their duties and ask for frequent leave of absence for long durations. Under these conditions it is not only difficult for them to keep abreast of the literature on the subject but they also lose the mental alertness which they displayed before marriage. Employers are, therefore, inclined to prefer men rather than women. However, under the present conditions when so many girls receive the M.Sc. and Ph.D. degrees in botany and zoology, and there are many unfilled jobs due to a scarcity of qualified men,

it might be desirable to institute part-time positions in which women scientists can work for three or four hours a day and then return to their family duties. Their talent, it seems, ought not to be wasted in these critical days when there are so few scientists available in the country. Here we are reminded of the vast number of women scientists, technicians and doctors in Russia, but of course the two forms of society are not the same. In Russia the children are brought up in day nurseries whereas we have adopted the cult of the family and maternal care.

SENDING STUDENTS ABROAD FOR HIGHER EDUCATION

Until about 15 years ago there were no great problems about Indian students going overseas. Those who got such opportunities considered themselves specially fortunate and there was general satisfaction about this. The numbers of these young men were small, they were usually financed by their parents, they had little opportunity for overseas employment, and they naturally returned home after completing their work in two or three years. Now the position is different. There are numerous fellowships in every advanced country and it is estimated that presently there are no less than 10,000 Indians studying abroad in the fields of science and technology alone.

Two points must be considered in this connection. One is the proper selection of the students to be sent abroad and the other is that of ensuring their return to serve the motherland. Apart from the students chosen by the Ministry of Education there are a good many who receive fellowships from other countries through their own efforts by correspondence with various professors and directors of research. Whereas some of these men are quite sincere and have definite objectives, others are not worried about the choice of the subject or of the professor but go abroad merely to increase their market value in comparison to those who remain in India. It is this aspect to which I wish to call special attention. There are adequate facilities now in many institutions in our own country for work leading to the doctor's degree and more are being developed at a rapid rate. Should not Indian students, therefore, go abroad only to seek such knowledge, techniques and experience as cannot be obtained locally? Should they not normally be post-doctoral scholars and persons holding appointments here to which they will return after working overseas for one or two years?

It is the considered opinion of many senior scientists that Indian students going abroad just to pass examinations and obtain foreign diplomas and degrees should be definitely discouraged from this attempt. It should be impressed on them and proper steps taken to ensure it that their market value will not increase merely by their doing elsewhere what can be done equally well in their own country. Secondly, the Universities and Institutes in India should be strengthened to take care of a larger number of students working for the doctor's degree and to improve the facilities for research in various branches. The third point is the choice of the subject. Many a time an Indian student has gone abroad for the study of some glamorous problem without any concern about the continuation of such work on his return to India. This naturally causes him a lot of frustration but it is largely his own fault. To remedy this evil, there should be Advisory Committees on an all India basis in different branches of science who will interview intending candidates and advise them as to the place and subject of their studies. Many American professors have spoken of the difficulty experienced by them in judging the relative merits of Indian scholars applying to them for fellowships and expressed the view that it would be a great help if a screening committee here would select only the best students for higher studies in the USA.

There is also another aspect of this foreign travel. There was a time in our history when scholars from various parts of Asia and Europe came to India to learn from the sages of the East. At present it seems that the trend is definitely reversed and we are continually sending our men even for work leading to the doctor's degree. This is obviously because our facilities and know-how are not up to the mark to attract notice in the more developed countries. However, it is entirely possible that students from some countries like Argentina, Egypt, Hungary, Indonesia, Japan, Malaya, Nigeria, Poland and Turkey may like to work here under some distinguished professors. But we have so far no way of subsidizing these scholars. While, Indian scholars get free board, lodging and tuition from our Big Brothers like the UK, USA, and Germany, is it not our duty in turn to do something for scholars from countries whose resources in men and materials are not even as good as ours? We are a part of the brotherhood of nations and we must do unto others what is being done for us.

Everything that is possible should be done to encourage this two-way traffic. We should set up fellowships for people coming from other countries if they require financial help and create facilities for their work. If there are institutes or departments which are able to attract foreign scholars by the excellence of their work, these need to be fostered with greater care than others. Admittedly, we cannot lead world sciences except in a few areas but wherever such areas exist these places should be more generously subsidized so that we also draw scholars from elsewhere and our prestige in science does not remain at its present low level.

THE SCIENTISTS' POOL

In order that the young scientist, who returns from abroad, does not feel stranded, the CSIR, under the Ministry of Education and Science, has constituted a Pool in which the monthly emoluments vary from Rs. 500 to 700 (sometimes more) plus the dearness and other allowances admissible to Class I officers of the CSIR. Theoretically, persons with Indian qualifications are also eligible but for all practical purposes the selection is limited to those returning from abroad. According to a recent decision of the Cabinet every eligible person is to be absorbed in the Pool.

While the objective is laudable, there are several points which need to be considered very carefully. In the first place this arrangement places a premium on a foreign doctorate and thus continues to draw people away from the country even in such cases where proper facilities exist in our own universities. It is a common experience that the best students with a first class Bachelor's and Master's degree immediately receive a fellowship of Rs. 250 per month from the CSIR, ICAR, UGC, Atomic Energy Commission or some other source, and usually remain in India while others who fail to receive such fellowships look for something outside the country. A good many of them go to the USA. On their return they receive a post in the pool on Rs. 600 or so whereas the students, who have taken their doctorate in this country and are often potentially more capable, are given only Rs. 400.

Further, the man who is in the Pool continues to draw his salary almost indefinitely. He has thus no inclination to apply for any but a Class I job or a Readership in the University. He is not willing to be considered for a Lecturership where the starting salary is only Rs. 400 per month. Usually he is not imme-

diately acceptable for a Readership or a Class I job but since he can remain in the Pool as long as he likes and with only some nominal work, it is no disadvantage to him. The result is that while there are many vacancies (sometimes 30 per cent of the total) in almost all institutions, they remain unfilled and the services of these young men remain unutilized.

The following steps are suggested to remedy the situation:

1. Although a pool post should be available immediately after a person's return from abroad, it may be provided on a one year basis during which time the beneficiary ought to find a place for himself. Normally a fresh Ph.D. should be given only Rs. 400 unless all post-doctoral fellowships and lecturerships in universities are advanced to Rs. 600. By starting the pool scientist on a higher basis, his chances for permanent and useful appointment are not improved but actually decreased. However, as I shall explain later, I would personally prefer all science posts for men with a doctorate or equivalent qualifications to be graded from Rs. 600 to Rs. 1800.

2. It is to be noted that most Directors of Institutes or Heads of University Departments are not too enthusiatsic about having Pool officers posted in their laboratories. It is feared that these men take it as a stop-gap arrangement and fail to make any substantial contribution. This matter needs to be examined more carefully to remove the difficulties, if any, in obtaining sufficient returns for the money spent on the scientists who ought to be encouraged and even prodded to do their best so that they are acceptable for a more useful and stable position as early as possible.

THE DISTRIBUTION OF OUR SCIENTIFIC EFFORT

There are various ways in which scientists may classify themselves. They could call their work as "pure" or "applied". They could designate themselves physicists, chemists, botanists, zoologists, anthropologists, engineers, doctors, and so on. Scientists are also called upon to act as administrators, as advisers in industrial organizations, as designers and as producers. How are we to judge whether our present emphasis on these respective fields is correct? Since we cannot be active at all points at once, gaps must exist in several places. The question is to find out which gaps are the most critical. These are the ones that must be rectified.

Unfortunately, no one seems to have made a careful assessment of our future requirements of scientists of different kinds based on the pattern of national development and economic growth during the next 10 or 15 years. While there may well be adequate freedom for the specially brilliant to follow any line of inquiry they please, there should be some reasonable basis for the distribution of our scientific effort. It is a difficult task and I do not think there can be any unanimity of opinion on this point. However, it does deserve some consideration by a group of scientists representing various lines of research.

To take an example, most people in India are hardly worried whether man lands on the moon in A. D. 1999 or A. D. 2200. On the other hand, we are all very much concerned about the problems of food and of overpopulation. Here I should like to quote Dr D. S. Kothari, Chairman of the University Grants Commission, as to our requirements in applied biology and agriculture : "For example, the percentage of agricultural students in the university population in

India is about the same as it is in the UK. It is much less than what it is, say, in the USSR, China or Japan. Modern agiculture is really applied biology. It is necessary in relation to our plans of agricultural development and increased food production that the effort on agricultural education should be very much more than what it is today".

Ladies and gentlemen, we pay much lip-service to the food problem but have we done anything substantial to solve it? If the input is so little, can we expect the output to be very large? If food, health and the control of population are our major problems today, is it not logical that greater attention be paid to them than to the other things for which there is less urgency?

Another distinguished physicist. J. D. Bernal, wrote as follows about the future of biology in his book entitled *Science in History*: "Growing, as it has, hardly less fast than have the physical sciences, it has had a far more rapid impact on society than they have had—except in the service of war . . . . . In the near future, given an end to the Cold War, the rewards of biology are bound to lead to its very rapid increase. At the same time its intrinsic interest will draw more and more able workers into biological studies. Apart from nuclear physics it is biology, and particularly biochemistry and biophysics, that are already the most exciting fields of research. This is because biology offers problems of great complexity where ingenuity is at a premium."

With 80% of the population engaged in agriculture this is easily our largest industry. Is it not important then that more attention be devoted to applied biology — extension work as well as research?

EMOLUMENTS

As pointed out already much of the competition in the modern world is a competition in scientific attainments. The most important investment of a country's revenue must, therefore, be in the scientists themselves. This point, I fear, is not sufficiently appreciated in India and is one of the reasons why many of our men are taking employments in foreign countries. There have been cases when Indian scholars came here to examine the possibilities of securing a suitable job but were disappointed and returned within a few weeks. It is difficult to estimate the number of Indian scientists and technologists staying abroad but assuming that it is only 5 per cent of the total, the trend is decidedly on the increase. An exposure to the wonderfully well equipped laboratories of the USA, a taste of their high standard of living, and the possibility of securing jobs carrying salaries many times as high as ours, all combine to act like a magnet on our young men and women. Let us understand that there is no point in accepting foreign aid if we are to export Indian talent in return.

While the situation here is not quite so serious as in Britain which seems to be losing 10-12% of its scientists to the USA, it demands consideration because of our perpetual dearth of good scientists and the fact that with our present rate of expansion many posts are already lying unfilled. A few suggestions are offered below to remedy this situation:

Since science and technology are admittedly the most important branches of knowledge in the modern world, special incentives must be provided by awarding scholarships of higher value in these subjects and further assuring that the pay and prospects will also be higher in these fields than in others. This is already being done in the USSR with great advantage. In India also professors in the

Medical and Engineering Colleges are being paid more than their counterparts in the pure sciences. However, if we need more scientists of all kinds, should they not be placed on par without sorting them in a differential pattern?

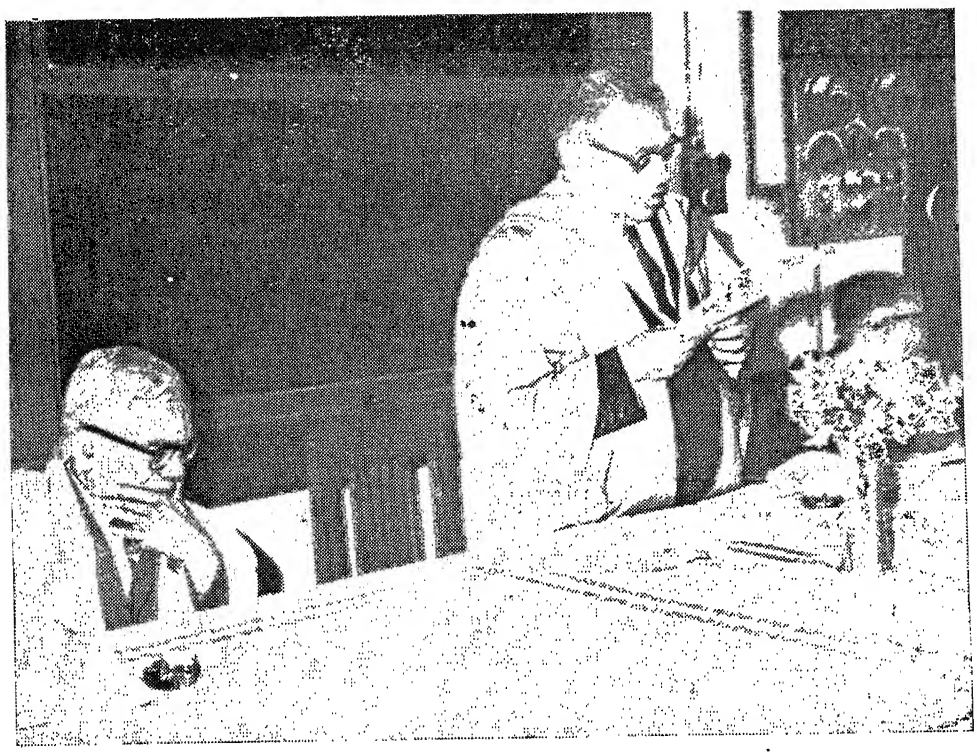
Young scientists all over the country complain about the lack of opportunities for advancement and about the big road-blocks that lie in their path no matter how good they may be. While this complaint is perhaps not fully justified it appears that the best solution would be to place all scientists with a doctorate or equivalent qualification after they have passed through a proper Selection Committee in one uniform scale of Rs. 600-1800 with three or four efficiency bars at suitable intervals when an expert committee would evaluate and assess their performance. Not all will cross these bars but the fact that the opportunity exists for every one to do so will surely put a person at ease and stimulate him into an effort which he may not be inclined to put in otherwise. For persons of exceptional merit there should be a further possibility of promotion to a grade of Rs. 1800-3000 so that the salaries of the best scientists are not below those in the administrative field. What justification can there be that the best brains in research be paid lower than those in administration? Unless this is done there will always be a tendency for the scientist to look wistfully to an administrative career.

The creation of a uniform scale of Rs. 600-1800 has many other advantages. To give an example, suppose that a person is serving in the Central Potato Research Institute on Rs. 600-1000 per month and a post is advertised in the Rice Research Institute on Rs. 700-1200, he would be glad to bury the potato and transfer his affections to rice. This would mean in effect that he will leave the crop with which he obtained some familiarity for one about which he knows nothing. While under ceretain circumstances such transfers are possible, effective work requires that such occasions be reduced to the minimum. This is easily achieved by providing the uniform scale mentioned above to all entrants in the scientific service.

A word may be said about the posts in the Universities. There is a general feeling that in selecting persons for higher jobs (say Readerships and Professorships) the age and experience of the candidate is a strong factor in his favour. Such a practice is extremely unsatisfactory, for the guiding criterion should be the ability alone. Experience comes automatically but intrinsic worth and creative talent are the result of heredity and hard work. The ideas which I have set forth about the creation of a uniform scale for scientists should also apply to the Universities but no real good will come unless the periodic assessments of the work of the candidate are made without fear or favouritism.

It was a good idea that the government set up some National Professorships for the most distinguished men in the Arts and Sciences. These are posts of honour carrying much higher emoluments than the usual professorial chairs and giving the holder considerable freedom as to the place or subject of his research without being bothered by administrative and other distractions. However, people are seldom elected to such positions until after they are 60-65 years old or more. While on the one hand it has been said that brilliant ideas seldom come after the age of 30-35 (in physical sciences) and 40-45 (in biological sciences), it seems strange that the National Professorships should be awarded at such a late age in life. One would think that 50—55 would be about the right age to spot the most gifted individuals so that they can be removed from administrative duties and permitted to spend the rest of their lives in purely creative work without the hinderances that beset the path of the overworked administrator. Further, it is

Dr. S. Bhagavantam delivering the Inaugural Address



Prof. P. Maheshwari delivering the Presidential Address

no compliment to Indian talent if in the whole country there are only some half a dozen persons qualified to be made National Professors in the entire field of knowledge including the Humanities and Sciences.

According to some persons it is good that there is now a competition for scientific talent all over the world. Many professors in the USA have said in private that if they hire scientists on good salaries from other countries this itself will perhaps force the latter (India among them) to pay their scientists well and to improve the conditions for their work. The slow, pedestrian manner in which things move in Asia makes one feel that perhaps they are right and it is only a thorough shake-up which will open the eyes of the public to the need for giving the scientists greater recognition than they have received so far.

Briefly then, while there must be no sympathy for laziness or indolence for a really talented person there should be no upper limit except the sky itself. With the introduction of a uniform grade of Rs. 600-1800 and the possibility of further advancement for men of exceptional merit no able person would have any fears about his future.

OUR DISINCLINATION TO WORK

Having presented a case for higher emoluments for scientists, it is now necessary to examine the other side of the question. Many visitors have remarked that India is a place with lowest wages and highest prices, that Indians are not serious about their work and that they are more interested in postpon ng things and in finding excuses for not doing a job. They are also said to be casual, unmethodical and slovenly in their behaviour and duties. If one were to visit any governmental or other office here and compare it with one in the UK or the USA such an impression does not appear unjustified. Nothing seems to move here without half a dozen reminders and personal interviews with officials at three or four levels. There is no sense of urgency in anything and each person passes the ball to the next without any one doing anything very tangible. However, at least a part of the blame must be shared by the senior officers themselves. Do they go in time if not before time to their respective offices and remain on until after 5 o'clock? How much time do they spend in celebrations and inaugurations of various functions and how much in actual work? Do the scientists themselves spend long hours of concentrated work in the laboratory and do they fully utilise their spare hours in thought and study and research?

While there should be a reasonable limit to the number of "periods" a scientist is called upon to devote to teaching, there can be no ceiling on the hours he may wish to devote to research work. Here the greater the time put in, the greater will be the rewards. A genius is the result of 90% perspiration and 10% inspiration. Is not personal example better than precept? If we, the older people, set a high example of devotion and spend regular hours of consistent research in the laboratory it is highly improbable that our younger colleagues and Ph. D. students would fail to respond. Let us remember the example of Gandhiji, the Father of the Nation, who was able to inspire millions of men and women to follow his noble example and make unheard of sacrifices in the cause of the country. If the proper example is not there, it will always be tempting for the juniors to sit and consume dozens of cups of tea instead of doing honest research.

Six ways come to my mind to stimulate research: (1) to select men with the best ability and experience for each post; (2) to provide a reasonably good

starting salary (say Rs 600 per month) to qualified persons who have done work of the doctoral standard; (3) to assure every one of the opportunities for professional advancement based on achivement and ability only; (4) to provide the necessary facilities such as space, equipment, technical help, and money for recurring expenditures (5) to make an impartial assessment of the work of every individual from time to time; and (6) to see that while the real worker is rewarded with special increments and a recognition of his efforts, the sluggards are ruthlessly weeded out.

I must explain my last point a little more fully. Permanency in a post is usually linked to our concept of academic freedom. This provides a person with the desired protection and freedom from worry which are so necessary for the pursuit of knowledge. However, quite often this security of tenure has itself become a shelter for incompetence and mediocrity. Once a man has been appointed, he feels himself a little too secure and prone to go even to a court of law for any action taken against him for his inability to deliver the goods.

It is this kind of a situation which is responsible to a large degree for the low output of research in our country. Although scientists are greatly valued in the USSR and paid much better than in other professions there is no permanency or security for them if their output is unsatisfactory. In the USA also there is no permanency for instructors and assistant professors who are appointed on a year to year basis. It is only after a man has been tried in such positions for at least five years that he may expect to get a tenure post such as an associate professorship.

Unless we can adopt some such system for assuring higher standards in making the initial appointments followed by longer and more closely supervised periods of probation, there is not much hope that we can greatly increase the quality of research in even the distant future. Depending on the assessment and evaluation of his work by a small committee, it should be possible to confirm the employee, or to demote him, or to give him special promotions.

THE HUMAN ELEMENT IN RESEARCH

Given even the most favourable conditions for research, with respect to both salary and equipment, it remains to be seen as to how the work of the young scientist is influenced by his surroundings, especially his colleagues and the Director of the institute.

It is a common experience that in the present-day set up the modern young man is often more conscious of his rights than of his obligations. Misunderstandings often arise about the authorship of a paper, There are complaints about Directors causing delays in forwarding the papers of their junior colleagues for publication. This is perhaps true in some cases and is to be regretted. Yet the sweeping statements often made these days of senior scientists exploiting their juniors are far from true. In fact senior scientists often give away much of their productive time only to create more opportunities for young people to work with them, take their doctorates, and then go into the wide world so that they can initiate others into the path of research. For a 'guru' it is a real pleasure to be excelled by his own pupil. Did not Dronacharya have his greatest satisfaction in having Arjun excel him in the art of archery and did not Arjun cherish a life-long reverence to his teacher?

It is to be regretted that the Director is himself rarely able to do any research work. He has to spend most of his time in making budgets; ordering equipment; signing contingency vouchers and salary bills; preparing schemes for the five year plans; interviewing candidates for his own institution and others; attending innumerable committee meetings at his own place and elsewhere; in giving lectures both inside and outside his organization; in editing journals; in scrutinizing papers for other journals; in replying to queries from various sources, both in India and outside; in sending, receiving and acknowledging reprints of publications; in consultations with his Ph.D. students and staff; and in scrutinizing several Ph.D. theses and research papers. He has to coordinate research work involving the participation of the several sectional heads under him and send periodical reports on it. He has also to spend a good bit of his time in diplomatic tussles, both above and below, in order to achieve his objectives.

All this and the difficulty of evoking a response from the authorities without a succession of reminders and personal contacts leaves him little time to do any active work. Not only this, unless he is extremely conscientious and hardworking he finds it difficult even to keep pace with the growing literature on the subject.

This is a sad state of affairs indeed for the primary role of the Head of a laboratory is creative, and not that of an accountant or administrator. All scientists called upon to do much work of this kind ought to be given effective technical assistance so that their time is not wasted with minor details and they are able to get a few hours every day for quiet study and thought and act as catalysers of research. It is a pity that our Universities and Government Institutes follow a penny-wise and pound — foolish policy in attaching so little value to the time of their top scientists. If they were merely to provide every Head of a large laboratory with an efficient administrative secretary on a pay of Rs. 500-800 per month they could save him from much harrassment and get much more creative work out of him than at present. In no industry would the management make the mistake of burdening its key men with petty jobs which can be done by persons of lower qualifications.

THE RED TAPE

Another disturbing factor to a research department is the severe limitation imposed on it both for cash purchases of petty articles and for ordering more costly apparatus. For cash purchases there seems to be a ceiling of Rs 20 per item and even for orders to be placed after calling numerous quotations and sealed tenders there is a limit of Rs 2,000 or so. For values beyond these, higher authorities are to be consulted irrespective of the availability of adequate funds.

This is an extremely short-sighted policy. In accordance with the present rise in prices, for cash purchase of any particular item the limit should be raised to Rs 100; and for orders for apparatus and equipment — once the usual formalities of calling for quotations and comparing them have been fulfilled — there should be no limit at all except the availability of funds. The present procedure is a great impediment in scientific work and a source of much frustration. Due to our involved procedure and inordinate delays in obtaining the goods, they are often sold out and once again one has to go through the process of inviting fresh quotations.

During recent years our troubles have only increased still further. Apart from the inevitable quotations and sealed tenders which have always been there one must now obtain a proforma invoice, an import licence, a 'not manufactured in India' certificate and so on. Each one of these is a long and arduous business and

all of them together would sap the vitality of any normal person. The period of waiting, in spite of numerous reminders at every level, extends to anything between 12 to 15 months. Meanwhile, the prices change and one may have to proceed all over again. Even photographic goods and drawing materials, so essential for biological work, have often been difficult o obtain in the open market. The whole system of accounting, internal and external auditing, and inviting sealed tenders for buying even a few chemicals, creates a sense of annoyance and disappointment, particularly in the minds of those returning from abroad who have seen their professors ordering costly articles merely by making a telephone call. To these people at least it appears that most of the officials and procedures in our country exist only to delay things until the arrival of the end of the financial year when the purse strings suddenly open from nowhere and there is a desperate hurry to squander what remains. This process has perforce converted many able heads of departments into mere accountants and fillers of forms.

FOREIGN EXCHANGE

While the red tape has been in existence for many years, additional difficulties have recently cropped due to the lack of foreign exchange. In a meeting of scientists, held in August, 1963, and presided over by the Minister for Scientific Research and Cultural Affairs, many distinguished scientists stressed the need for more foreign exchange to buy special apparatus and equipment. However, no appreciable progress has been made in this direction. These difficulties still persist not only for the purchase of new equipment but even for the repair of existing instruments. To take an example, even if only the lenses of a microscope require resetting and polishing one has to go through pretty nearly the same involved procedure as for buying a new item.

Foreign exchange is also urgently needed for buying books and periodicals, for sending membership fees to learned societies, and for purchasing reprints of papers published in foreign journals. Many scientists have experience of the delays and annoyance caused to them even in these minor matters and the supercilious manner in which the Government officials sometimes treat them. If scientists cannot be paid better, can they not at least be shown more consideration in these matters?

Sometimes an Indian scientist is invited to contribute a paper to a Congress held abroad and even to preside over a part of its deliberations. It would be ungrateful not to acknowledge the support our Government has given to many persons with regard to their transport but the greatest difficulties are created even for an allowance of £50 or so to maintain the scientist for a few days in a foreign country. The result is that he has to exist on the charity of others and put himself into a humiliating not only for himself but also for his country just because of the lack of a few pounds or dollars. Such restrictions are inconsistent with our concepts of academic freedom. Whatever the stringencies, will a young and emotional scientist continue to have respect for his country if he is sent away to a distance of 10,000 miles with a bare Rs 25-75 in his pocket while any number of "cultural" missions consisting of dancers and musicians travel all over the world without hinderance? These are little things but it is a dozen pinpricks of this nature which affect a man more than one major item. He thereby becomes a stranger to his own land and transfers his loyalty to the country which gave him some small support in his hour of need.

In the meeting of scientists held on August, 4, 1963, Professor Humayun Kabir, then Minister for Scientific and Cultural Affairs, was constrained to remark as follows :

> "When one considers the figures involved, it is surprising that there should be bottle-necks of this type. The total requirement of foreign exchange for equipment for technical training has been estimated at about Rs 110 million for the whole of the Third Five Year Plan. For research laboratories also the figure is about Rs 100 million for the whole Third Five Year Plan. In other words, less than Rs 250 million is required for equipment for training and research for the whole of the Third Five Year Plan and yet this amount is not always readily available. Can there be any defence for this when we are receiving foreign aid at the level of about Rs 6,000 million a year exclusive of the value of exports?"

I would not be surprised if the degree of vexation involved in obtaining equipment abroad is even known to the senior officers in the Secretariat. I shall recapitulate it below so that public opinion is mobilised in the matter and speedy action taken to remedy the situation. At the outset we must wait for the announcement of release of foreign exchange (this usually trickles in a few hundreds of rupees from time to time) by the UGC to the Registrar of the University and from the Registrar to the Heads of the Departments. The time taken for this is about three months. After this the Head of the Department obtains proforma invoices for such equipment or apparatuses as can be obtained within the value sanctioned for his department. He must then send two copies of the import licence applications together with 9 copies of a detailed list of the goods to the Registrar who will secrutinise them and send them over to the UGC. The UGC will now send these applications to the Development Wing of the Ministry of Commerce and Industry for clearance from the "indigenous angle" and to certify that the equipment is not manufactured in India. The papers are now returned to the UGC which sends them on to the Chief Controller of Imports and Exports in the Ministry of Commerce and Industry. If the licence is now issued, it begins its journey back through the UGC and the Registrar to the Head of the Department.

However, in most cases the licence comes in an incomplete form as the original list of goods is misplaced or lost. The licence is, therefore, rendered void and you begin your correspondence again by sending new copies of the lists. Often the letter of authority in favour of the firm is missing. After the complete licence comes back, the agent of the desired firm may be contacted and orders placed for the equipment with the manufacturers abroad. By now, however, the manufacturers may have put out a new model or the prices have changed. If this happens, a long correspondence starts afresh.

The ordeal is by no means over. The scientist has to enter into a new correspondence through the normal stepwise channels with the Development Wing to issue a fresh "Not Manufactured in India" Certificate. This makes a mockery of the earlier clearance of the import licence applications from the "indigenous angle". More annoying still is the fact that the Customs authorities are not satisfied with this certificate and applications have to be made to the Ministry of Education for a "Customs duty exemption certificate". After a year's correspondence one may well find that while one Ministry has given the necessary certificate the other refuses to do so. The duty has, therefore, to be paid and another year-long correspondence initiated for its refund.

By now the scientist may have given up all plans for research and may have taken another job, or returned to a foreign country!

Ladies and gentlemen! Is it not the duty of the authorities concerned to make every effort to simplify these procedures and reduce the delays so as to save time for productive work rather than involve themselves and others in petty affairs which can be left to themselves?

CONCLUSION

In conclusion, I wish to say that while our Government spends a great deal more money on science than ever before and this is appreciated by all lovers of the country, that is not enough. The investment on science and on foreign exchange for scientific research must be greatly enhanced and greater consideration shown to the scientist himself than even to the laboratories and to the equipment which are merely the tools for his research. We must extend our concepts of academic freedom. This means freedom to work, freedom to publish, freedom to go abroad to attend congresses and meet one's colleagues, freedom to buy instruments and literature, and freedom to do other academic jobs without being compelled by poverty into inactivity. I am quite certain, ladies and gentlemen, that the government under the leadership of our respected Prime-Minister will give the scientists what they deserve and raise their status in the country to a much higher level than it is at present. It will of course be our duty in return to do what we can to remove hunger, to increase the output of our farms and factories, and to win adequate recognition for our country in the world of science. I would appeal to all Indians who have taken jobs abroad to return to the place of their birth and to serve it even at a sacrifice. We have made sacrifices in the past; shall we not make similar and greater sacrifices in the future? It is true that science is international but we are Indians first and everything else afterwards.

JAI HIND!

ABSTRACTS OF PAPERS

1. Stereochemistry of Carvomenthols and Related Compounds

G. S. SIDHU, *Regional Research Laboratory, Hyderabad-9*

The conformations of the four stereo-isomeric carvomenthols were studied by Johnston and Read in 1934 when rules of conformational analysis were not well established. Later workers have used these assignments in correlating other terpenoids and therefore have arrived at some incorrect conformational assignments. In this paper the inconsistencies of Johnston and Reads' work are pointed out and the necessity to assign the correct conformations to the isomeric carvomenthols and related compounds is emphasised.

2. Saponins and Sapogenins XX—Chemical examination of the seeds of Pithecolobium dulce, Benth (Inga dulcis Willd.)

I. P. VARSHNEY *and* K. M. SHAMSUDDIN, *Department of Chemistry, Aligarh Muslim University, Aligarh*

The seeds of Pithecolobium dulce Benth, obtained from Kerala, on defatting and alcohol extraction gives a mixture of saponins, which on sulphuric acid hydrolysis gives the sapogenins. On acetylation and fractional crystallisation it has been shown to contain Proceric acid, acetate m.p. 286-83°; acetyl methyl ester m.p. 269-74° (cf. Proceric acid acetate m.p. 288-90°; acetyl methyl ester m.p. 268-70° earlier isolated from Albizzia procera seeds from Maharashtra) and an unidentified acid genin, acetate m p. 215-22°; acetyl methyl ester m.p. 217-22°.

3. Saponins and Sapogenins XIX—The study of the Sapogenin from the seeds of Albizzia stipulata, Boiv.

I. P. VARSHNEY, *Department of Chemistry, Muslim University, Aligarh*

The seeds of Albizzia stipulata, Boiv. from Maharashtra, yield a colourless saponin, which on sulphuric acid hydrolysis gives a genin; m.p. 270-71°, acetate m.p. 231-32°. It has been identified as acacic acid by mixed melting point and infra-red spectra. Acacic acid has been suggested to have β-amyrin type structure on chemical and biogenetic grounds.

4. Chemical Examination of the Leaves of Sesbania grandiflora (Linn.) : Isolation and Study of a Sapogenin.

R. D. TIWARI *and* R. K. BAJPAI, *Department of Chemistry, University of Allahabad, Allahabad*

The ethanolic extract of the leaves of Sesbania grandiflora (Linn.) Pers. yields a saponin which on acid hydrolysis furnishes an acid sapogenin m.p. 300-302° and galactose, rhamnose and glucuronic acid. The sapogenin has been identified to be oleanolic acid (3 β—hydroxy – Δ^{12} – oleanene – 28 oic acid).

5. Extractives from Bark and Wood of Diospyros Melanoxylon

G. S. SIDHU *and* A. V. B. SANKARAM, *Regional Research Laboratory, Hyderabad-9*

Petroleum ether extraction of the bark and the sapwood of Diosppyros melanoxylon (Roxb) yielded five crystalline constituents. Four of these have been identified as β -sitosterol, lupeol, betulin and betulinic acid. The presence of phenolic and quinonoid compounds in the extractives of the heartwood has been revealed by thin layer chromatography. Further work is in progress.

A recent report by Row *et al.*[1] describing the isolation of lupeol and betulin from the same source has prompted us to make this communication.

1. *Ind. J. Appl. Chem.*, **6**, 28 (1963).

6. Isolation and Study of the Mucilage from the Fruit of Cordia Myxa Linn.

R. D. TIWARI *and* PURNIMA DAVE, *Department of Chemistry, University of Allahabad, Allahabad*

The defatted pulp of the Cordia Myxa fruit was extracted with water and the mucilage precipitated with ethanol, repeating this procedure several times to obtain a product with minimum ash content. Preliminary analysis of the purified mucilage gave - methoxyl 5·28 %; uronide 15·7 % ; acetyl 4·17 % and ash 12·6 %. Hydrolysis of the mucilage and paper chromatographic examination of the hydrolysate revealed the presence of D-galactose, L-arabinose, D-xylose, D-galacturonic acid and an unidentified sugar resembling deoxy-hexoses. Quantitative estimation of the sugars were carried out by paper chromatography followed by elution and periodate oxidation giving D-galactose 31·8 %, D-xylose 12·9 % and L-arabinose 19·83 %. Repeated methylation with dimethyl sulphate and sodium hydroxide followed by Purdie's reagents gave a methylated product which was fractionated into three fractions. These fractions on hydrolysis gave 2, 3, 4, 6-tetra-O-methyl-D-glactose ; 2, 3, 6-tri-O-methyl-D-galactose ; 2, 4-di O-methyl-D-galactose, 2-O-methyl-L-arabinose ; 2, 3, 4, -tri-O methyl-D-xylose and 2, 3-Di-O-methyl, D-galacturonic acid. On the basis of these a structure for the mucilage has been suggested.

7. Chemical Examination of the seed Mucilage from Thespesia Populnea Soland

S. N. SRIVASTAVA, V. N. SHARMA *and* K. N. KAUL, *National Botanic Gardens, Lucknow*

Kaempherol and its glycoside (originally designated as populenetin and popunin respectively) along with herbacetin were reported[1,2,3] to have been isolated from the petals and the flowers of *Thespesia populnea* Soland. Recently[4], another new colouring matter, provisionally named thespesin, $C_{19}H_{20}O_5$, has been isolated from the fruits and a tentative structure has been assigned to it as a flavanone with three hydroxyl groups and a C_4H_9-chain in unlocated positions. The present communication deals with the results of studies of the seed mucilage.

Successive hydrolysis of the mucilage obtained from the fresh, air dried seeds of *T. populnea* Soland. with 3 per cent oxalic acid, 2 N sulphuric acid and concentrated sulphuric acid yielded arabinose, xylose, galactose and aldobionic acid and galactose, xylose, rhamnose, arabinose and galactouronic acid and glucose respectively.

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1. Neelkantam K. and Sheshadri T. R , *Curr. Sci.*, **7**, 16 (1938).
2. Rao, P. R. and Sheshadri, T. R., *Proc. Ind Acad. Sci.*, **24A** 456 (1946).
3. Rao, P. S. and Reddy, P. P., *Proc. Ind. Acad. Sci.*, **12A**, 372 (1940).
4. Srivastava, S. N., Bhakuni, D. S. and Sharma, V. N., *Ind. Jour. Chem* , **1**, 451 (1963).

8. Chemical Examination of the Mucilage of the Seeds of Hygrophila spinosa

R. D. Tiwari *and* Sudha Kumari Agarwal, *Chemistry Department, University of Allahabad, Allahabad*

The mucilage of Tal Makhana (Hygrophila spinosa) was isolated by extraction with water and precipitation with ethanol. Purification of the mucilage was done by dissolving it in water and precipitating with ethanol and repeating this process till the ash content was reduced to a minimum.

On a priliminary analysis the purified mucilage gave the following results.

Ash	...	...	14·07 %
Methoxyl	...	...	3·00 %
Acetyl	...	...	1·38 %
Pentoses	...	...	17·093 %
Equivalent weight		...	2231
Uronide content...		...	33·42 %

On hydrolysis with 2N sulphuric acid (18 hrs) a monosaccharide xylose (Rf 0·18) and an oligosaccharide (Rf 0·043) in butanol:ethanol:water:ammonia (40:10:49:1) was obtained, the same two sugas were obtained when the mucilage was hydrolysed by formic acid (98 — 100 %) (7 hrs) or by N sulphuric acid (30 hrs). The oligosaccharide Rf 0·048 also contains the uronic acid part of the mucilage and is such that it resists hydrolysis by all the above reagents. A detailed examination of the oligosaccharide is in progress.

9. New Colouring matters from Cassia tora Linn

R. K. Sharma *and* P. C. Gupta, *Chemical Laboratories, University of Allahabad, Allahabad*

Three new colouring matters obtained from the fat soluble brown deposit from the seeds of Cassia tora Linn have been found to belong to anthraquinone group of colouring matters. The three colouring matters have been provisionally named

Tora colouring matter A, shining red-orange flakes m.p. 236–38°, Tora colouring matter B dark-red crystalline compound m.p. 196-98° ; and Tora colouring matter C, yellow crystalline substance m.p. 230-32°. The three colouring matters are definitely anthraquinone derivatives as anthracene is obtained by Zn-dust distillation of the colouring matter A while Zn-dust distillation either of the colouring matter B or the colouring matter C yields 2-methyl anthracene which is further confirmed by IR peaks characteristic to anthraquinone or its hydroxy derivatives at 1686 cm^{-1}, 1678 $cm.^{-1}$ and 1660 cm^{-1} given by the respective colouring matters. As regards the orientation of the substituent groups in the different colouring matters, attempts have been made on the basis of characteristic colour reactions, some chemical tests and IR given by the individual colouring matters.

10. Chemical Examination of the Coloured Compounds from Casia alata

R. D. Tiwari *and* Tila Joshi, *Chemical Laboratories, Allahabad University, Allahabad*

Three different coloured compounds (I) $C_{13}H_8O_4$ yellow m.p. 164° (II) $C_{15}H_{10}O_4$ dark yellow m.p. 194° and (III) $C_{17}H_{14}O_6$ red m.p. 212 have been isolated from the seeds of Casia alata. The yellow compound $C_{15}H_{10}O_4$ has been found to be identical with Chryso. The structures of the other two compounds are being studied.

11. Chemical Examination of Litsea Consimilis—Nees-Study of Alkaloids

K. L. Dhar *and* R. N. Singh Chauhan, *Chemical Laboratories, Th. D. S. B. Government College, Nainital*

An alkaloid Laurotetanine $C_{19}H_{21}O_4N$. H_2O, m.p. 125°, has been isolated from the bark and the seeds of *Litsea Consimilis*. A hydrocarbon m.p. 214°, probably a triterpenoid has been also isolated from the seeds of the plant.

12. Chemical Examination of Fraxinus Floribunda - Study of Glycosides—Part I

K. L. Dhar *and* R. N. Singh Chauhan, *Chemical Laboratories, Th. D. S. B. Government College, Nainital*

Presence of three glycosides was found in the bark of *Fraxinus floribunda*—for which no analytical data is found in any standard journal. As such one coumarin glycoside m p. 187° was isolated, which on hydrolysis gave a glucone $C_9H_6O_4$ (a dihydroxy coumarin). A good yield (about 1%) of mannitol was also obtained. By papyrographic method, glucose was found to be the sugar portion of the glycoside.

13. Chemical Examination of *Fraxinus floribunda*—Study of Glycosides—Part II

K. L. Dhar *and* R. N. Singh Chauhan, *Chemical Laboratories, Th. D. S. B. Government College, Nainital*

The glycoside m.p. 187° isolated from the bark of *Fraxinus floribunda* (reported earlier) has been found to be an impure Cichoriin m.p. 210° found in

the flowers of *Cichorium intybus*. Two more glycosides were also isolated from the bark of the tree and were identified as Fraxin m.p. 200°-205° and Aesculin m.p. 200-205°. Both cichoriin and aesculin on hydrolysis gave an aglucone aesculitin. Identity of aesculitin was established by the study of its properties, mixed m.p., study of absorption spectra and chromatographic studies.

14. Chemical Study of Chenopodium ambrosoides Linn.

G. S. Gupta *and* S. P. Bhatnagar, *Chemistry Department, Muslim University, Aligarh*

The local variety of the plant which grows wildly in the Aligarh District, yields on steam distillation an essential oil (0·22 %) with a smell resembling that of the plant. The physico-chemical properties of the oil have been studied. The oil contains carbonyl compounds (16 %) and phenolic products (30 %) and has been found to consist of ascaridole (17 %) and *p*-cymene as the main constituent. Fatty oil has been obtained from the dried seeds, and a saponin has been isolated from the seeds and roots of the plant. A compound $C_{30}H_{62}O$, m.p. 82-84°, has been obtained from the petroleum-ether and alcoholic extracts of the seeds and appears to be *n*-triacontanol. Further work is in progress.

15. Structure of Nimbin

N. S Narasimhan, *Department of Chemistry, University of Poona, Poona-7, and* C. R. Narayan, K. V. Pachapurkar, S. K. Pradhan *and* V. R. Shah, *National Chemical Laboratory, Poona-8*

Nimbin, the crystalline compound obtained from *Melia indica*, has the molecular formula $C_{30}H_{36}O_9$ and the following functional groups-one $\alpha\beta$-unsaturated cyclic ketone having two cis hydrogen atoms, two methoxycarbonyls, one acetate of a secondary alcohol on a six member ring, one ether, one double bond carrying a methyl group, one β-monosubstituted furan, and a total of four C-methyl groups. It would appear to be a pentacyclic tetranortriterpene.

Recently the structure of several tetranortriterpenes, biogenetically derived from euphol have been elucidated. The similarity of certain features of nimbin with them indicates that nimbin also belongs to this series of compounds. A closer examination of the chemical and physical properties of nimbin and its degradation products, however, reveals one novelty about the structure of nimbin, which is, that in it the C-ring of the triterpenoid precursor is biogenetically opened.

A structure for nimbin is discussed which is in harmony with all the known reactions and properties of nimbin and its degradation products.

16. Chemical Examination of *Terminalia paniculata* Roth

R. M. Beri *and* M. G. Karnik, *Chemistry of Forest Products Branch, Forest Research Institute, Dehra Dun*

Analyses of *Terminalia paniculata* bark shows that it is made up of 27 per cent of extractives that can be removed by successive extraction with petroleum either, chloroform, alcohol and water. 28 per cent of carbohydrate, 33 percent of 'lignin'

and 9·6 per cent of ash. The bark does not contain any alkaloids. It contains 14 per cent of tannins, which have a pyrogallol nucleus in the molecule rather than a catechol nucleus along with gallic acid. β-sitosterol has been isolated and identified from the petroleum either extract of the bark.

17. Lactone from Salvia haematodes (Lalbahman)

S. N. KHANNA *and* P. C. GUPTA, *Chemical Laboratories, University of Allahabad, Allahabad*

On cooling and keeping the hot ethanolic extract of the roots of Salvia haematodes over night, a dirty white deposit settles down which on crystallisation from hot ethanol yields a white crystalline substance m. p. 62°. It is soluble in hot alkali and reprecipitated on acidification and it develops an intense yellow colour in ethanolic caustic potash. It has been characterised and found to be an unsaturated lactone. It quickly decolourises alkaline potassium permanganate solution but a bromine solution either in carbon tetrachloride or chloroform is decolourised a bit slowly. It yields an acetyl derivative m. p. 57°, a methyl ester m. p. 74°C and a bromo derivative m. p. 60°C.

18. Some minor constituent acids of Lac Resin

S. C. SEN GUPTA, *Indian Lac Research Institute, Namkum, Ranchi*

Lac resin is believed to be composed of a mixture of aliphatic and hydroaromatic hydroxy acids which are present as cross-linked polyesters. The presence of aleuritic acid and its isomer (30-35%), butolic acid (5-8%), shellolic acid (3-4%), *epi*-shellolic acid and jalaric acid (~25%) have been proved with certainty. The present paper describes the isolation and identification, by various chromatographic techniques, of a few straight chain aliphatic acids such as tetra- hexa- and octa-decanoic acids, a mixture of tetradecenoic acids, hexa- and octa- dec-9-enoic acids, 16-hydroxyhexadecanoic acid, 16-hydroxyhexadec-*cis*-9-enoic acid and 6-ketotetradecanoic acid. The presence of 9, 10- and 9, 16-dihydroxyhexadecanoic acids have also been established.

19. The Fatty Acid Composition of the Feronia elephantum trunk bark fat

R. D. TIWARI, P. D. SATTSANGI *and* K. C. SRIVASTAVA, *Department of Chemistry, University of Allahabad, Allahabad*

The fat isolated from the trunk bark of Feronia elephantum, on examination has been found to contain the glycerol and β-sitosterol esters of the palmitic, stearic, oleic and linoleic acids. The percentage distribution of these acids is:—

Palmitic	...	3·71 %
Stearic	...	5·42 %
Oleic	...	87·13 %
Linoleic	...	3·74 %

This is in agreement with the observation that the bark fats usually consist of oleic acid as the major component along with smaller amounts of palmitic and stearic acids.

20. The Study of the Component acids from the seed fat of Luffa echinata

K. C. Srivastava, *Chemical Laboratories University of Allahabad, Allahabad and* J. P. Tiwari, *Department of Pharmacology, G. S. V. M. Medical College, Kanpur*

The fatty acid composition of the Luffa echinata seed fat was studied by two different methods: firstly by the liquid solid counter current distribution of the mixed acids with urea and secondly by the resolution of the mixed acids by the lead salt alcohol method followed by low pressure fractionation of their methyl esters. The results obtained by these two methods agree broadly and on the whole resemble the fatty acid composition of the seed fats from the family Cucurbitaceae. The percentage composition is as follows:—

	Palmitic	Stearic	Oleic	Linoleic
Urea method	20·71	8·11	36·74	34·44
Distillation method	19·14	7·44	33·00	40·42

21. Application of Mass Spectrometry in Alkaloid Studies

S. C. Pakrashi, *Indian Institute for Biochemistry and Experimental Medicine, Calcutta*

Recent applications of mass spectrometry in the structural and stereochemical problems of various types of alkaloids will be reviewed with special reference to the work related to the author's own laboratory.

22. Semimicro Determination of Saponification Equivalents of Higher Fatty Acid Esters

R. D. Tiwari *and* J. P. Sharma, *Department of Chemistry, University of Allahabad, Allahabad*

Micro and semimicro determination of neutralization equivalents of higher fatty acids has been reported earlier by the authors. The method has been further extended for the semimicro determination of saponification equivalents of methyl esters of higher fatty acids. It has been observed that while dealing with fats and fat products, some times one comes across with smaller quantities of the products and in such a case the analysis of the product becomes difficult with usual macro methods.

20-30 mg of the sample was accurately weighed in a pyrex glass vial and transferred to a flask which had arrangement for passing Nitrogen gas. An excess of ethanolic potossium hydroxide (10 ml of 0·02 N) was added and heated for 1/2 hr under reflux, passing nitrogen gas all the time through the flask. After 1/2 hr, the contents were cooled and the excess alkali back titrated against standard solution of methanolic hydrogen chloride using 3-4 drops of the mixed indicator (A mixture of 0·4% methanolic solutions of Phenol red, Cresol red and Bromothymol blue in the ratio of 3 : 1 : 1).

A blank determination was simultaneously carried out, under identical conditions.

Determinations carried out with the esters of lauric, myristic and palmitic acids showed that the results were accurate to within $\pm$ 1% of the theoretical values.

23. Estimation of Alcoholic Constitutents and Esters in Essential oils and Synthetic Mixtures, Part XIV

J. B. LAL *and* B. S. RAWAT, *Chemical Engineering and Technology Department, Harcourt Butler Technological Institute, Kanpur*

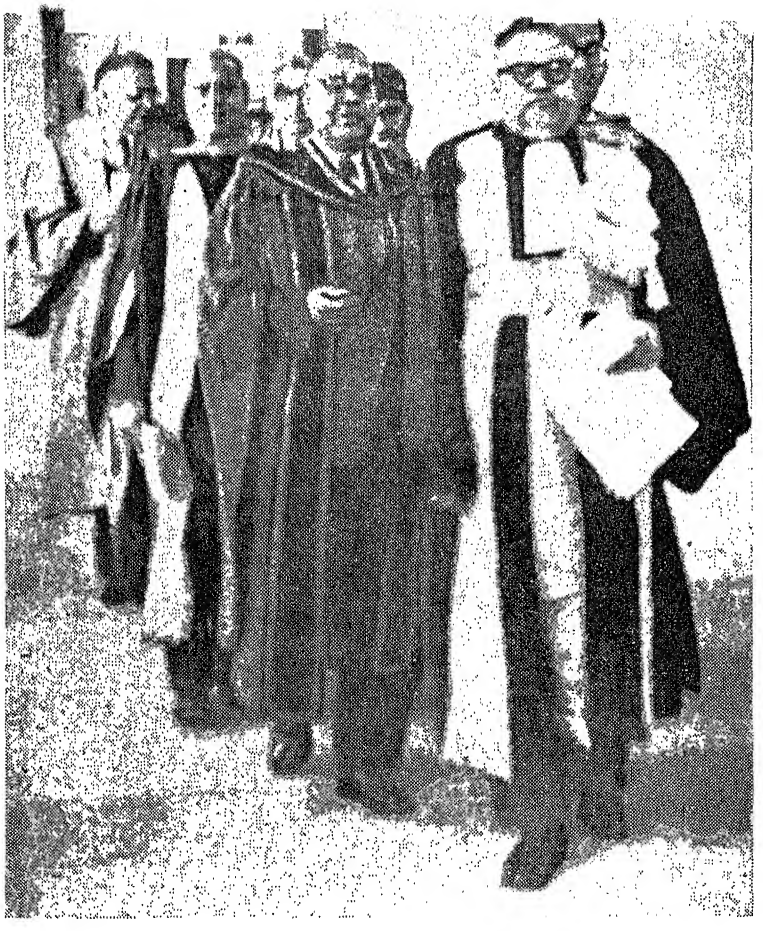
In the present investigation the work has been carried out on the applicability of the three formulae in the estimation of alcohol in essential oils and synthetic mixtures. The authors have shown that the formula L_4 derived by them gives better results in comparison to the Ramanathan's formula L_1 in case the acetylated mixture is washed with brine solution containing sodium carbonate so as to be completely free from acids originally present in the essentia oil. Whereas the Cocking's formula L_2 and the formula L_3 are equivalent and give the same result when the acetylated product is washed with brine solution only.

24. Studies on Plant Latex

RADHA PANT *and* S. C. SRIVASTAVA, *Biochemistry Section, The University, Allahabad*

The proteolytic activity of fourteen samples of latex obtained from different plants has been studied. The pH optima of five samples of latex have been determined. *Calotropis gigantes* and *Carica papaya* have 6 as their pH optima and *Ficus carica* 5. It is interesting to note that the fresh crude latex of *Calotropis procera* and *Cryptostegia grandiflora* exhibit two distinct peaks of activity at pH 4 and 8 and 5 and 7 respectively. Appearance of these two peaks at different pH suggests the presence of two components possessing proteinase activity in these two samples of latex.

The latex of *Calotropis procera* yielded a compound of the composition $C_{17}H_{28}O$. From this compound, a sterol has been obtained which has been subjected to acetylation, benzoylation and oxidation.



Members of the Council entering in a procession.

SYMPOSIUM ON LAND FERTILITY, IMPROVEMENT AND ALKALI SOIL RECLAMATION BY BLUE GREEN ALGAE

1. Presidential Address by Prof. N. R. Dhar, Director, Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.
2. On certain features of the Blue-green Algae and their relation to the nitrogen-status of the environment by A. K. Mitra, Department of Botany, University of Allahabad, Allahabad.
3. Reclamation of Alkali Soils by blue green algae by C. L. Dhawan, Land Reclamation, Irrigation and Power Research Institute, Amritsar.
4. Physiological studies on a nitrogen fixing blue green algae by H. D. Kumar, Department of Botany, University of Gorakhpur, Gorakhpur.
5. Effect of algae in nitrogen fixation in black cotton soils by N. R. Dhar and P. G. Deo, Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.
6. Influence of light intensity, organic matter and phosphates on nitrogen fixation and phosphate availability in presence or absence of algae by N. R. Dhar and G. N. Bhat, Sheila Dhar Institute of Soil Science, University of Allahahad, Allahabad.
7. Retarding effect of algae on nitrogen loss from black cotton soils when treated with fertilizers by N. R. Dhar and P. G. Deo, Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.
8. Influence of Algae in composting by N. R. Dhar and S. P. Jaiswal, Sheila Dhar Institute of Soil Science University of Allahabad, Allahabad.
9. Influence of Algae in alkali soils by N. R. Dhar and G. P. Srivastava, Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.
10. Retarding effect of algae in loss of nitrogen from Allahabad Soils by N. R. Dhar and A. K. Rishi, Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.
11. Influence of straw and basic slag in checking nitrogen loss in absence or presence of algae by N. R. Dhar and A. K. Rishi, Sheila Dhar Institute of Soil Science, University of Allahabad. Allahabad.

12. Algal culture in organic wastes by A. C. Gaur, Division of Chemistry Indian Agricultural Research Institute, New Delhi.

13. Oxidation pond effluents and their role in land fertility J. S. S. Lakshminarayana and M. Parabrahman, Central Public Health Engineering Research Institute, Nagpur.

14. Pixation of elementary nitrogen by *Scytonema hofmanni* and Fischerella muscicola in pure and unialgal cultures by V. K. Laloraya, Department of Botany, University of Allahabad, Allahabad.

15. Studies in Chlorella by H. Tamiya, The Takugawa Institute for Biological Research, Tokyo (Japan).

16. Studies on the blue green algae as green manure in Japan by A. Watanabe, Institute of Applied Microbiology, University of Tokyo, Tokyo (Japan).

17. Composting of water hyacinth in presence and absence of algae by N. R. Dhar and B. S. Gupta, Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.

18. Influence of algae on the yield of paddy in Ramnagar, Allahabad by N. R. Dhar and D. N. Sharma, Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.

APPENDIX I

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2. Acta Biologica Cracoviensia: Botanica (Slawkowske, Poland)
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4. Acta Biologica Venezuelica (Cracas, Venezuela)
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15. Biologiske Skrifter det Konglige Videskabernes Selskab (Copenhagen, Denmark)
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21. Bulletinul Institution Politechnic din Issi (Lasi R. R., Romania)
22. Candian Journal of Biochemistry (Ottawa, Canada)
23. Canadian Journal of Botany, (Ottawa, Canada)
24. Canadian Journal of Chemistry, (Ottawa, Canda)
25. Canadian Journal of Physics (Ottawa, Canada)
26. Canadian Journal of Zoology, (Ottawa, Canada)
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31. Endeavour (London, England)
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33. German Research Service (Bad Godes berg, Germany)
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54. New Zealand Journal of Science (Wellington, Zew Zealand)
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76. World Meteorological Organisation (Geneva, Switzerland)

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4. Ganita (Lucknow)
5. Half-yearly Journal of Mysore University (Mysore)
6. Indian Journal of Agricultural Science (New Delhi)
7. Indian Journal of Chemistry (New Delhi)
8. Indian Journal of Experimental Biology (New Delhi)
9. Indian Journal of Meteorology and Geophysics (Delhi)
10. Indian Journal of Physics (Calcutta)
11. Indian Journal of Pure and Applied Physics (New Delhi)
12. Indian Journal of Technology (New Delhi)
13. Indian Journal of Veterinary Science and Animal Husbandry (New Delhi)
14. Indian Minerals (Calcutta)
15. Journal of Indian Chemical Society (Calcutta)
16. Journal of Indian Institute of Sciences (Bangalore)
17. Journal of Scientific and Industrial Research (New Delhi)
18. Proceedings of the Indian Academy of Sciences, Section A and B (Bangalore)
19. Proceedings of National Institute Sciences of India, Section A and B (New Delhi)
20. Research Bulletin of Punjab University (Chandigarh)
21. UNESCO Chronicle (New Delhi)
22. Vijnana Parishad Anusandhan Patrika (Allahabad)

APPENDIX III

LIST OF MEMBERS AND FELLOWS

(Completed upto 1st June, 1964)

[*Names of Fellows are marked with**; *and of Life Members with* †]

Agarwal, G. P., M.Sc., D.Phil., Lecturer in Botany, Government Science College, Jabalpur.

†Agarwal, Ved Prakash, M.Sc., Ph.D., Professor and Head of the Zoology Dept., D.A.V. College, Muzaffarnagar.

Ahmad, Z. U., M.Sc., Senior Research Assistant, Section of the Plant Pathologist to the Government U. P., Kanpur.

†Ahuja, Bhopindra Singh, M.Sc., Botanist, Survey of Medical Plants, Government of India Project, P.O. Gurukula Kangri (Dt. Saharanpur).

Agnihotri, Virendra Prasad, M.Sc., c/o Agnihotri Engineering Works, Rudrapur, Naini Tal.

Ambasht, J. P., M.Sc., F.R.A.S., Head of the Mathematics Department, S. P. Jain's College, Sasaram. (Dt. Shahabad) Bihar.

Ambasht, R. S., M.Sc., Lecturer in Botany, Banaras Hindu University, Varanasi-5.

†Arora, R. K., M.Sc. (Hons.), Ph.D., Assistant Ecologist, Botanical Survey of India, 76 Lower Circular Road, Calcutta-14.

†Awasthi, P. N., M.Sc., D.Phil., Assistant Professor of Chemistry, University of Saugar, Sagar.

Bagalkoti, D. R., M.Sc., Ph.D., Head of the Physics Dept., Karnatak Regional Engineering College, Surathkal, S. K.

Bagchi, A. K., B.A. (Hons.), 'Amrapati', Indian Statistical Institute, 204 Barrackpore Trunk Road, Calcutta-35.

*Bagchi, H. D., M.A., Ph.D., Peary Mohan Sur Lane, Goabagan, P.O. Beadon Street, Calcutta-6.

†Bahadur, K., M.Sc., D.Phil., D.Sc., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

Ballabh, Ram, M.Sc., Ph.D., Professor and Head of the Department of Mathematics, University of Lucknow, Lucknow.

*Banerjee, D. P., M.A., D.Sc., F.S.S., Professor and Head of the Department of Mathematics, Sri Venkateswara University, Tirupati (A. P.).

*†Banerjee, K., D.Sc., F.N.I., F.I.A.S., Director, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32.

*†Banerji, A. C., M.A., M.Sc., F.R.A.S., F.N.I., I.E.S. (Retd.), Gyan Kutir, 4 A-Beli Road, Allahabad-2.

†Banerji, N. K., M.Sc., D.Phil., Senior Research Fellow, Sheila Dhar Institute of Soil Science, University of Allahabad, 2 D-Beli Road, Allahabad-2.

*Banerji, S. K., D.Sc., F.A.Sc., M.A.E.S.I., Hon.F.R.Met.Soc., 3 Ramani Chatterjee Road, P. O. Rashbehari Avenue, Calcutta-29.

*†Banerji, S. K., M.Sc., D.Phil., Reader - Head, Chemistry Department, Birla College of Engineering, Pilani (Rajasthan).

*Banerji, S. N., M.Sc., D.Phil., Reader in Chemistry, University of Saugar, Sagar.

Basu Chaudhary, K. C., M.Sc., Ph.D., Associate Professor of Botany, Agra College, Agra.

*†Basu, S., M.Sc., F.N.I., Retired Director General of Observatories, L-25 Hauz Khas Enclave, New Delhi-16.

†Baugh, S. C., M.Sc., Ph.D., Assistant Professor of Zoology, University of Lucknow, Lucknow.

*Behari, Ram, M.A., Ph.D., Sc.D., F.N.I., F.A.Sc., Director, Directorate of Correspondence Courses, University of Delhi, 32 Probyn Road, Delhi-6.

Bhagwat, W. V., D.Sc., Principal and Professor of Chemistry, Holkar Science College, Indore.

†Bhanot, V. B., M.Sc., Ph.D., Reader in Physics, Panjab University, Chandigarh-3.

Bharadwaj, O. N., M.Sc., Lecturer in Zoology, Holkar Science College, Indore (M.P.).

Bhardwaj, S. N., M.Sc., Ph.D., F.B.S., Asst. Plant Physiologist, Division of Botany, Indian Agricultural Research Institute, New Delhi-12.

*†Bhargava, H. R., M.Sc., F.B.S., Assistant Professor of Botany, University of Saugar, Sagar.

*Bhargava, K. S., M.Sc., D.Phil., Ph.D., Professor and Head of the Botany Department, University of Gorakhpur, Gorakhpur.

†Bhargava, S. N., M.Sc., D.Phil., Botany Department, University of Allahabad, Allahabad.

Bhatia, Prem Kumar, M.Sc., Ph.D., Lecturer in Mathematics, University of Jodhpur, Jodhpur.

Bhatia, B. B., B.V.Sc. & A.H., M.V.Sc., Research Officer (Parasitology), U. P. College of Veterinary Science and Animal Husbandry, Mathura.

Bhatnagar, A. N., M.Sc., D.Phil., Lecturer in Zoology, D. A. V. College, Dehra Dun,

Bhatt, B. D., M.Sc., c/o Śri R. D. Bhatt, Naya Bazaar, Nainital.

*†Bhattacharya, A. K., D.Sc., F.R.I.C., Professor and Head of the Department of Chemistry, University of Saugar, Sagar.

†Bhattacharya, Abani K, D.Sc., F.R.I.C., Professor and Head of the Post-Graduate Department of Chemistry, J. and K. University, Jammu (Kashmir).

Bhattacharya, A. P., M.A., Research Officer, Basic Research Division, Irrigation Research Institute, Roorkee.

Bhattacharya, Arun K., M.Sc., Ph.D., Asst. Professor of Chemistry, University of Saugar, Sagar.

Bhattacharya, P. K., M.Sc., Ph.D., Lecturer in Chemistry, University of Rajasthan, Jaipur.

*†Bhawalkar, D. R, M.Sc., Ph.D., Professor and Head of the Department of Physics, University of Saugar, Sagar.

Bhise, Vinayak Madhav, M.Sc., Lecturer in Mathematics, Govindram Seksaria Technological Institute, Opp. Nehru Park, Indore.

Bhonsle, B. R., M.Sc., Ph.D., Professor of Mathematics, Govt. Engineering College, Jabalpur (M. P.).

*Bilgrami, K. S., M.Sc., D.Phil., D.Sc., Reader in Botany, University of Jodhpur, Jodhpur.

*†Biswas, B., M.Sc., Maewal Compound, Nawabganj, Kanpur.

*†Bose, K. C., M.Sc., D.Phil., Professor and Head of the Department of Zoology, Ranchi University, P. Box No. 11, Ranchi.

*Bose, Sameer, M.Sc., Ph.D, 310 Napier Town, Near Christian High School, Jabalpur.

*†Chakravarti, B., M.Sc., D.Phil., Agfa Photopaper Co., Mulund, Bombay-80.

*†Chakravarti, S. C., M.Sc., Ph.D., Principal, Government Degree College, Mhow (M. P.).

†Chakravarty, D. N., M.Sc., D.Phil., National Carbon Company, 5 Rustomji Parsee Road, Calcutta-2.

Chandra, Jagdish, M. A., Department of Mathematics, Mason Labs., Rensselaer Polytechnic Institute, Troy, N. Y. (U.S.A.).

Chandra, Sudhir, M.Sc., D.Phil., Department of Botany, University of Allahabad, Allahabad.

Chandra, Sudish, M.Sc., Research Scholar, Chemistry Department, University of Lucknow, Lucknow.

*†Chatterjee, A. C., D.Sc., Dr.Ing., Vice-Chancellor, University of Gorakhpur, Gorakhpur.

Chatterjee, Peetendu, M.Sc., Asst. Manager, Durrung Tea Estate - Modopee Division, P.O. Bindukuri, Dt. Darrang (Assam).

†Chatterji, P. N., M.Sc., D.Phil., Department of Zoology, G. M. College, Sambalpur (Orissa).

*†Chatterji, R. G., M.Sc., D.Phil., Department of Physics, Indian Institute of Technology, Kharagpur.

*†Chatterji, U. N., D Phil., D.Sc., F.R.S.A., Professor and Head of the Botany Department, University of Jodhpur, Jodhpur.

*†Chauhan, B. S., Ph.D., D.Sc., C.H.Z.S., F.A.Sc., F.Z.S.I., Superintending Zoologist, Zoological Survey of India, 34 Chittaranjan Avenue, Calcutta-12.

Chauhan, R. N. Singh, M.Sc., D.Phil., Asst. Professor of Chemistry, Th. D.S.B. Government College, Nainital.

Chauhan, Suresh Kumar, M.Sc., Ph.D., Lecturer in Botany, Agra College, Agra.

*Chinoy, J. J., M.Sc., Ph.D., D.I.C., Head of the Department of Botany, Gujarat University, Ahmedabad.

†Chitray, Brij Behari, M.Sc., Head of the Biology Dept., H.S.J.S. College, Kanpur.

*†Chopra, Col. Sir R. N., C.I.E., M.D., Sc.D., F.R.C.P., Director, Regional Research Laboratory, Jammu and Kashmir, Canal Road, Jammu-Tawi, Kashmir.

Chopra, R. S., M.Sc., Reader in Botany, Panjab University, Amritsar.

*Choudhari, R. S., M.Sc., Ph.D., D.Sc., Reader in Agricultural Botany and Physiologist, College of Agriculture, Banaras Hindu University, Varanasi-5.

*†Chowdhary, H. S., M.Sc., D.Phil., Professor and Head of the Department of Zoology, University of Gorakhpur, Gorakhpur.

Choudhuri, D. K., M.Sc., Ph.D., D.I.C., Lecturer in Entomology, University of Kalyani, P. O. Mohanpur, Dt. Nadia, West Bengal.

*†Chowdhury, K. A., B.A., B.Sc., M.S., D.Sc., F.N.I., Professor and Head of the Botany Department, Muslim University, Aligarh.

Dalela, G. G., M.Sc., Ph.D., Junior Specialist, Plant Pathology Section, Department of Agriculture, Rajasthan, Udaipur.

Das, Niranjan, M.Sc., D.Phil., Assistant Professor of Botany, University of Allahabad, Allahabad.

*†Das, S. M., D.Sc., F.Z.S., F.A.Z., F.Z.S.I., Professor of Zoology, Jammu and Kashmir University, Srinagar, Kashmir.

*†Das Gupta, S. N., Ph.D., D.Sc., D.I.C., F.N.I., Vice-Chancellor, University of Kalyani, 1 B Judge's Court Road, Calcutta-27.

Datta, Bimalendu, M.Sc., Asst. Zoologist, Zoological Survey of India, 34 Chittaranjan Avenue, Calcutta-12.

*†Dave, J. S., M.Sc., Ph.D., A.R.I.C., Reader in Physical and Inorganic Chemistry, Faculty of Science, M. S. University, Baroda.

David, A., B.Sc., D.Sc., Tank Blocustine Unit of the Central Inland Fisheries Research Institute, Tungabhadra Dam P. O. (Mysore State).

Davis, T. A., B.A., P.G.Dip. (Crop Bot.), Professor of Crop Science, Indian Statistical Institute, Calcutta-35.

*Dayal, Bisheswar, D.Sc., F.Inst.P., A.I.I.Sc., Reader in Physics, Banaras Hindu University, Varanasi-5.

Dayal, Ram, M.Sc., D.Phil., Department Pathology, College of Agriculture, Banaras Hindu University, Varanasi-5.

†Dehadrai, P. V., M.Sc., F.G.S., F.G.M.S., M.M.G.I., Senior Petrologist, Oil and Natural Gas Commission, Government of India, 19 Rajpur Road, Dehra Dun.

†De, Samarenda Kumar, B.Sc.Ag., M.Sc. (Ag. Bot.), M.Sc. (Ag. Chem.), D.Phil., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

*†Deodhar, D. B., M.Sc., Ph.D., Anand Niwas, Havelock Road, Lucknow.

*†Dey, A. K., B.Sc. (Hons.), M.Sc., D.Phil., D.Sc., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

*†Dey, P. K., M.Sc., I.Ag.S. (Retd.), 53/1 Southern Avenue, Calcutta-29.

†Dhar, A. K., M.Sc., Assistant Agricultural Officer, Ramnugger Cane and Sugar Co., Ltd., Plassey, District Nadia (W. B.).

*Dhar, M. L., M.Sc., Ph.D., F.R.I.C., F.N.I., Director, Central Drug Research Institute, Chattar Manzil Palace, Lucknow.

*†Dhar, N. R., D.Sc., F.R.I.C, F.N.I. I.E.S. (Retd.), *Associate Member of the French Academy of Agriculture* and *Correspondirg Member of the French Academy of Sciences*, Director, Sheila Dhar Institue of Soil Science, University of Allahabad, 2 D-Beli Road, Allahabad-2.

*†Dhawan, C. L., M.Sc., Ph.D., Deputy Director, Land Reclamation, Irrigation and Power Research Institute, Amritsar.

*†Doosaj, S. S., M.Sc., Principal, Govt. College, Satna (M. P.).

†Dugar, S. M., M.Sc., Research Scholar, Department of Chemistry, University of Rajasthan, Jaipur.

*†Dutta, S. K., D.Sc., 57 Tarakutir Road, Lukerganj, Allahabad.

Dwivedi, R. S., M.Sc., Ph.D., Lecturer in Botany, Banaras Hindu University, Varanasi-5.

Gandhi, J. N., M.Sc., Reader and Head of the Physics Department, Maharani's College, Jaipur.

†Garg, N. K., M.Sc., D.Phil., Ph.D., Division of Biochemistry, Central Drug Research Institute, Lucknow.

*†Gayre of Gayre and Nigg, Lt. Col. Robert, K.C.N., K.C.M.M., K.C.L., G.C.L.J., M.A., D.Phil., D.Pol.Sc., D.Sc., F.I.A.L., 1 Darnaway Street, Edinburgh-3 (Scotland).

†Ghadially, P. F., F.R.G.S., F.R.S.A., F.B.H.I., B.Sc., M.M.E.A., A.M.I.E., M.I.S.D., Messrs. Precists (India) Private Ltd., 43 Queen's Road, Bombay-2.

Ghoshal, Satish Chandra, B.A., B.Sc., LL.B., Retired Director of Education, Indore and Alwar States, 8 Vikramaditya Marg, Lucknow.

*†Ghosh, S., D.Sc., F.N.I., Professor and Head of the Department of Chemistry, University of Jabalpur, Jabalpur.

*†Ghosh, S. C., M.Sc., D.Phil., Assistant Professor of Zoology, University of Allahabad, Allahabad.

*†Ghosh, S. K., M.Sc., D.Phil., Assistant Agricultural Chemist to the Government of West Bengal, State Agricultural Research Institute, 230 Netaji Subhas Road, Tollygunge, Calcutta-40.

*†Ghosh, S. N., D.Sc., Professor of Applied Physics, J. K. Institute of Applied Physics, University of Allahabad, Allahabad.

†Gill, P. S., M.S., Ph.D., M.A.P.S., F.N.I., Director, Central Scientific Instruments Organization, Chandigarh.

Goyal, A. N., M.Sc., Ph.D., F.R.A.S., Lecturer in Mathematics, Maharaja's College, Jaipur.

Goyal, G. K., M.Sc., Lecturer in Mathematics, University of Rajasthan, Jaipur.

†Grover, (Miss) Prabha, M.Sc., D.Phil., 14 Park Road, Allahabad-2.

†Gupta, A. B., M.Sc., Ph.D., Head of the Botany Department, Christ Church College, Kanpur.

*†Gupta, A. C., B.Sc., F.H.B.T.I., F.R.I.C., Professor of Oil and Allied Technology, Harcourt Butler Technological Institute, Kanpur.

Gupta, D. R., M.Sc., Ph.D., Reader in Chemistry, University of Roorkee, Roorkee.

Gupta, K. C., M.Sc., Lecturer in Mathematics, University of Rajasthan, Jaipur.

†Gupta, Munendra Nath, M.Sc., Ph.D., F.B.S., Associate Professor of Botany, Agra College, Agra.

Gupta, R., M.Sc., Department of Zoology, Kanya Kubja College, Lucknow.

Gupta, R. K., M.Sc., Ph.D., Dr.es Sciences, Research Officer, c/o French Institute, P. O. Box 33, Pondichery.

†Gupta, S. C., M.Sc., Ph.D., D.I.C., F.B.S., Professor and Head of the Botany Dept., K. N. Govt. Degree College, Gyanpur (Dt. Varanasi).

Gupta, S. L., B.Sc. (Hons.), M.Sc., Lecturer in Mathematics, Faculty of Engineering, University of Jodhpur, Jodhpur.

Gupta, Y. K., M.Sc., D.Phil., Reader in Chemistry, University of Rajasthan, Jaipur.

*†Gyani, B. P., M.Sc., Ph.D., Principal, Ranchi College, Ranchi.

Gyanvati, D.Phil., Junior Scientific Officer, Defence Research Laboratory (Stores), Kanpur.

*Handa, K. L., M.Sc., F.R.I.C., F.I.C., Senior Scientific Officer, Regional Research Laboratory, Jammu (Kashmir).

Hariharan, T. A., M.Sc., Ph.D., Lecturer in Physics. Karnataka Regional Engineering College, Surathkal P. O. (S. K.) Mysore State.

Hasija, S. K., M.Sc., Lecturer in Botany, Govt. Science College, 457 Napier Town, Howbagh, Jabalpur.

Jain, K. D., M.Sc., Ph.D., A.R.I.C., Professor and Head of the Chemistry Department, D.A.V. College, Dehra Dun.

Jain, M. K., M.Sc., Lecturer, Chemistry Department, D.A.V. College, Dehra Dun.

*†Jain, S. K., M.Sc., F.B.S., Economic Botanist, Botanical Survey of India, 76 Lower Circular Road, Calcutta-14.

†Jain, S. L., M.Sc., Ph.D., Geological Studies Unit, Indian Statistical Research Institute, 203 Barrackpore Trunk Road, Calcutta-35.

Jaitley, (Miss) Priyamvada, M.Sc., D.Phil., Lecturer in Zoology, Govt. Hamidia College, Bhopal.

*Jhingran, A. G., M.Sc., Ph.D., F.N.I., F.G.M.S., M.M.G.I., Director, Eastern Region, Geological Survey of India, 5 Middleton Street, Calcutta-13.

Johri, L. N., D.Sc., Reader in Zoology, University of Delhi, Delhi-6.

*Joshi, A. C., D.Sc., F.N.I., Vice-Chancellor, Panjab (India) University, Chandigarh-3.

Joshi, N. C., M.Sc., Ph.D., F.B.S., Asst. Systematic Mycologist, Directorate of Plant Protection, 4/19 Ajmeri Gate Extension, New Delhi.

Kahate, Sindhu, M.Sc., Lecturer in Botany, Kamla Nehru Hall for Women, University of Jodhpur, Jodhpur.

*†Kapoor, R. C., M.Sc., D.Phil., D.Sc., Professor and Head of the Department of Chemistry, University of Jodhpur, Jodhpur.

Kapur, J. N., M.A., Ph.D., Professor and Head of the Mathematics Department, Indian Institute of Technology, Kanpur.

*Kar, B. K., Ph.D., F.B.S., 39/1 Puddopukur Road, Calcutta-20.

Kaushic S. D., M.A., Ph.D., Professor and Head of the Geography Department, S. S. V. College, Hapur.

†Khan, Reayat, M.Sc., Ph.D., Department of Botany, Aligarh Muslim University, Aligarh.

Khandekar, P. R., M.A., Professor of Mathematics, M. V. Mahavidyalaya, Bhopal (M. P.).

†Kothari, Hemraj, B.Sc., D.W.P., A.C.C.G.I., A.M.S.E., F.C.I., F.B.I.S., I.M.I. Consit. E., A.M.A.I.M., Management and Technical Consultant and Chief Executive, Kothari Consultants, 12 India Exchange Place, Calcutta-1.

Koul, M. L. Hakoo, M.Sc., Research Scholar in Botany, Banaras Hindu University, Varanasi-5.

*†Krishna, Bal, M.Sc., D.Phil., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

Krishna, Daya, M.Sc., D.Phil., Professor and Head of the Department of Zoology, Govt. College, Ajmer.

Krishnamurthy, K. N., B.Sc. (Hons.), Research Assistant, Central Inland Fisheries Research Institute, P. O. Tungabhadra Dam, Dt. Bellary, Mysore State.

†Kumar, Ram M.Sc., Ph.D., D.Sc., Professor of Mathematics and Head of the Department of Applied Mathematics, Applied Science and Humanities, M.L.N. Regional Engineering College, Allahabad.

*†Kushwaha, R. S., M.Sc., D.Phil., Ph.D., Professor and Head of the Department of Mathematics, University of Jodhpur, Jodhpur.

*†Lakhanpal, R. N., M.Sc., Ph.D., F.B.S., Assistant Director, Birbal Sahni Institute of Palaeobotany, University Road, Lucknow.

†Lakshmikanth, V., M.A., Professor of Mathematics, Marathawada University, Aurangabad.

†Lakshminarayana, G., M.A., Ph.D., Asst. Professor of Mathematics, Regional Engineering College, Warangal (A. P.).

Lakshminarayana, K. V., M.Sc., Asst. Zoologist, Zoological Survey of India, 34 Chittaranjan Avenue, Calcutta-12.

Lal, J. B., D.Sc., B.S.E. (Chem. Engg.), M.S.E., F.I.C., M.I. Chem.E., Head of the Chemical Engineering Section and Industrial Chemist to the U. P. Government, H. B. Technological Institute, Kanpur.

Lal, K. B., M.A, Ph.D., Assistant Professor of Mathematics, University of Gorakhpur, Gorakhpur.

Lal, M. B., M.Sc., Ph.D., M.A., LL.B., Head of the Zoology Dept., D.A.V. College, Dehra Dun.

Lall, S. B., M.Sc., Ph.D., Lecturer in Botany, College of Agriculture, Nagpur.

Loiwal, S. D., M.Sc., D.Phil., Asst. Professor of Chemistry, Birla College, Pilani (Rajasthan).

*†Mahabale, T. S., B.A., M.Sc., Ph.D., F.N.I., F.A.Sc., F.B.S., Head of the Department of Botany, University of Poona, Ganeshkhind, Poona-7.

†Mahajani, A. V., M.Sc., Ph.D., Assistant Professor of Chemistry, University of Saugar, Sagar.

*Mahalanobis, P. C., M.A., I.E.S. (Retd.), F.R.S., F.N.I., Director, Indian Statistical Research Institute, 204 Barrackpore Trunk Road, Calcutta-35.

*Maheshwari, P., D.Sc., F.N.I., F.B.S., F.A.Sc., Professor and Head of the Botany Department, University of Delhi, Delhi-6.

*†Majumdar, K., D.Sc., 20 Minto Road, Allahabad-2.

Majupuria, T. C., M.Sc., Ph.D., Head of the Zoology Department, M. S. (Post-graduate) College, Saharanpur.

*Malik, W. U., M.Sc., Ph.D., D.Sc., Professor and Head of the Chemistry Department, University of Roorkee, Roorkee.

*†Mani, M. S., D.Sc., Deputy Director, Zoological Survey of India, 34 Chittaranjan Avenue, Calcutta-12.

Mathur, B. L., M.Sc., Ph.D., Asst. Plant Pathologist, Plant Pathology Section, A-30 Tilak Nagar, Jaipur.

Mathur, B. P., M.Sc., c/o Dr. Tara Shanker Mathur, Brij Kutir, Arvind Marg, Jaipur.

Mathur, Daya Swarup, M.Sc., D.Phil., Birla College, Pilani (Rajasthan).

*†Mathur, K. N., D.Sc., F.Inst.P., Director, Central Scientific Instrument Organisation, C.S.I.R. Building, Rafi Marg, New Delhi-1.

†Mathur, P. B., M.Sc., D.Phil., Senior Scientific Officer, Central Electrochemical Research Institute, Karaikudi-3 (S. India).

Mathur, R. S., M.Sc., Ph.D., Assoc. I.A.R.I., Plant Pathologist to Government, U. P., Agricultural Gardens, Kanpur.

*†Mattoo, B. N., M.Sc., Ph.D., D.Sc., Senior Physicist, Forensic Science Laboratory, Government of Maharastra, Bombay-1.

*†Mehra, H. R., M.Sc., Ph.D., F.N.I., 33 Chatham Lines, Allahabad-2.

*Mehra, P. N., D.Sc., F.N.I., F.B.S., Professor and Head of the Department of Botany, Panjab University, Chandigarh-3.

†Mehra, Ram Krishna, M.Sc, Assistant Professor of Zoology, University of Allahabad, Allahabad.

*†Mehrotra, A. P., M.Sc., D.Phil., F.B.S., P.E.S.(I), Professor and Head of the Department of Botany, D. S. B. Government Degree College, Nainital.

*Mehrotra, B S., M.Sc., D.Phil., Assistant Professor of Botany, University of Allahabad, Allahabad.

Mehrotra, P. N., M.Sc., 60 Circular Road, Ranchi (Bihar).

*†Mehrotra, R. C., M.Sc., D.Phil., Ph.D., F.R.I.C., F.N.I., Professor and Head of the Department of Chemistry, University of Rajasthan, Jaipur.

Mehrotra, R. S., M.Sc., Ph.D., Asstt. Professor of Botany, University of Saugar, Sagar.

*Mishra, R. S., M.Sc., Ph.D., D.Sc., F.N.I., Professor and Head of the Department of Mathematics, University of Allahabad, Allahabad.

*Misra, M. L. D.Sc., Professor and Head of the Department of Mathematics, University of Saugar, Sagar.

*Misra, R., M.Sc., Ph.D., F.B.S., F.N.I., Professor and Head of the Department of Botany, Banaras Hindu University, Varanasi-5.

*†Misra, R. C., M.Sc., Ph.D., F.G.M.S., M.M.G.I., F.P.S., Professor and Head of the Department of Geology, University of Lucknow, Lucknow.

*†Misra, R. D., M.A., Ph.D., Member, Public Service Commission, U. P., 2-A Pannalal Road, Allahabad-2.

†Misra, S. G., M.Sc., D.Phil., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

*†Mitra, A. K., M.Sc., Ph.D., Reader in Botany, University of Allahabad, Allahabad.

†Mukerji, G. P., M.Sc., Department of Zoology, M. V. Mahavidyalaya, Bhopal (M. P.).

*†Mukherji, M. K., M.Sc., Ph.D., Division of Agricultural Chemistry, Jute Agricultural Research Institute, P. O. Nilganj Bazar, Barrackpore (W. B.).

†Mukherji, P. K., M.Sc., Lecturer in Botany, S.F.S. College, Nagpur.

*†Mushran, S. P., M.Sc., D.Phil., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

Nagar, S. K., M.Sc., 18 Telegraph Traffic Place, Baird Road, New Delhi.

Naik, Y. G., M.Sc., Ph.D., Principal Professor of Physics and Dean of the Faculty of Science, Gujarat College, Ahmedabad.

Nair, G. U., M.Sc., Research Assistant, Botany Department, Christ Church College, Kanpur.

Narain, Udai, M.Sc., Head of the Botany Department, Rajendra College, Chapra.

*Narlikar, V. V., M.A., F.R.A.S., F.N.I., F.A.Sc., Chairman, Rajasthan Public Service Commission, 7 Jaipur Road, Ajmer.

*†Nath, Raj, Ph.D., D.I.C., F.N.I., Professor and Head of the Department of Geology, Banaras Hindu University, Varanasi-5.

*†Nigam, S. S., M.Sc., Ph.D., D.I.C., Reader in Chemistry, University of Saugar, Sagar.

Oak, Mr. Justice V.G., B.Sc. (Hons.), I.C.S., 1 A-Beli Road, Allahabad-2.

*†Pal, N. L., D.Sc., Plant Physiologist, Central Tobacco Research Institute, Rajahmundry.

*†Pandey, B. P., D.Sc., Professor of Parasitology, U.P. College of Veterinary Science and Animal Husbandry, Mathura.

Pandey, Ravi, M.Sc., Head of the Department of Zoology, C.M.D. Degree College, Bilaspur (M. P.).

Pandeya, S. C., M.Sc., Ph.D., Reader in Botany, University School of Sciences, Ahmedabad-5.

Panigrahi, Gopinath, B.Sc. (Hons.), M.Sc., Ph.D., Regional Botanist, Central Circle, Botanical Survey of India, 10 Chatham Lines, Allahabad-2.

*Pannikar, N. K., M.A., D.Sc., F.A.S., F.N.I., F.Z.S.I., Director, Indian Programme, Indian Ocean Expedition, Council of Scientific and Industrial Research, Rafi Marg, New Delhi-1.

*†Parija P., M.A., D.Sc., F.N.I., F.A.Sc., I.E.S.(Retd.), Vice-Chancellor, Utkal University, Vani Vihar, Bhubaneswar (Orissa).

Patel, Vishnu Shankar, M.Sc., Asstt. Professor of Chemistry, J. H. Government Degree College, Betul (M. P.).

Pathak, Hari Datt, M.Sc., Assistant Professor of Chemistry, D.S.B. Government College, Naini Tal.

Patil, Ramakant Pandurang, B.A., M.Sc., Ph.D., Botanist, Central Botanical Laboratory, 43 Lansdowne Road, Calcutta-20.

*†Paul, Ram Chand, M.Sc., Ph.D., F.R.I.C., Professor and Head of the Chemistry Department, Panjab University, Chandigarh-3.

*†Perti, O. N., M.Sc., D.Phil., Professor and Head of the Department of Chemistry, D. S. B. Government Degree College, Naini Tal.

Prakash, Nam, M.Sc., c/o Shri Agun Prasad, Kaillawallen Street, Delhi Gate, Ghaziabad.

*†Prakash, Ved, M.Sc., Principal, Nehru College, Ajronda, Faridabad (Punjab).

*Prasad, Balbhadra, D.Sc., F.N.I., Vice-Chancellor, University of Allahabad, Allahabad.

*†Prasad, B. N., M.Sc., Ph.D., D.Sc., F.N.I., Laxmi Niwas, Lowther Road, George Town, Allahabad-2.

†Prasad, B. N., M.Sc., Ph.D., F.L.S., F.B.S., Department of Botany, University of Lucknow, Lucknow.

*†Prasad, Mata, D.Sc., F.R.I.C., F.N.I., Mathura Niwas, 4281 Pipal Mandi, Agra.

*Prasad, Sarju, M.A., M.Sc., D.Sc., Reader in Chemistry, Banaras Hindu University, Varanasi-5.

Prasad, S. S., M.Sc., Head of the Botany Departments, L. S. College, Muzaffarpur (Bihar).

*Puri, V., M.Sc., D.Sc., F.B.S., F.A.Sc., F.N.I., Professor and Head of the Botany Department, Meerut College, Meerut.

†Purohit, D. N., M.Sc., Research Scholar, Department of Chemistry, University of Rajasthan, Jaipur.

Purushottam, G., M.A., Department of Mathematics, Science College, Osmania University, Hyderabad-Dn. 7 (A. P.).

Raghuvanshi, S. S., M.Sc., D.Phil., Assistant Professor of Botany, Lucknow University, Lucknow.

Rajvanshi, S. C., M.Sc., Lecturer in Mathematics, Faculty of Engineering, University of Jodhpur, Jodhpur.

*†Rai, M.M., M.Sc., D.Phil., Professor of Chemistry, Government Agricultural College, Jabalpur.

Rai, P., B.V.Sc.&A.H., M.V.Sc., Assistant Professor of Parasitology, U. P. College of Veterinary Science and Animal Husbandry, Mathura.

†Rai, Rama Shanker, M.Sc., D.Phil., Post-doctoral Research Associate (A.E.C.), Radiochemistry Laboratory, Chemistry Department, Washington University, St. Louis 30, Mo. (U.S A.).

Rai, S. L., M.Sc., Research Scholar, Zoology Department, Mahakoshal Mahavidyalaya, Jabalpur.

Rai, U. K., M.Sc., D.Phil., Pulses Specialist, Agricultural Research Institute, P. O. Kanke, District Ranchi (Bihar).

Ramakrishan, P. S., M.Sc., Ph.D., Department of Botany, Panjab University, Chandigarh.

*†Ramamoorthy, B., M.Sc., D.Phil., Assoc. I.A.R.I., Physical Chemist, Division of Chemistry, Indian Agricultural Research Institute, New Delhi-12.

Raman, S. S., M.Sc., Ph.D., Lecturer in Botany, Banaras Hindu University, Varanasi-5.

Ramaswamy, K. R., B.Sc. (Hons.), M.Sc., Ph.D., Lecturer in Zoology, Karnatak University, Dharwar (Mysore).

*†Ramdas, L. A., M.A., Ph.D., F.N.I., F.A.Sc., F.R.Met.Soc., National Physical Laboratory, New Delhi-12.

*†Ramiah, K., M.Sc., D.Sc. (Hony.), F.N.I., F.A.Sc., Swathi, 552 XIX Cross Road, Bangalore-12.

*Ranade, J. D., M.Sc., Ph.D., A.Inst.P., Assistant Professor of Physics, University of Saugar, Sagar.

*†Randhawa, M. S., M.Sc., D.Sc., F.N.I., I.C.S., Adviser (Resources), Planning Commission, New Delhi-1.

*†Ranjan, S., M.Sc., D.Sc., F.N.I., F.A.Sc., 10 A-Beli Road, Allahabad-2.

Rao, A. L. Jagannadha, M.Sc., Lecturer in Chemistry, Punjabi University, Patiala (Punjab).

Rao, D. Rama Krishna, M.A., Lecturer in Mathematics, Department of Technical Education, Nehru Nagar, Secunderabad (A. P.)

Rao, K. M., M.A., Department of Mathematics, J. T. S. Govt. Polytechnic Vijayawada (A.P.).

Rao, M. Rama Mohana, M.A., Lecturer in Mathematics, College of Engineering, Osmania University, Hyderabad-7.

†Rao, S. N., M.Sc., Ph.D., F.R.E.S., F.A.Z., Head of the Zoology Department, Madhav College, Ujjain.

Rao, V.V.L.N., M.A., Reader in Mathematics, Osmania University, 1-5-106 Mushirabad, Hyderabad-Dn.20.

*Rawat, J. S., M.Sc., Ph.D., Assistant Professor, Department of Physiology and Biochemistry, U. P. College of Veterinary Science and Animal Husbandry, Mathura.

*Raychaudhuri, S. P., M.Sc., Ph.D., D.Sc., F.R.I.C., F.N.I., Senior Specialist (Land Resources), Planning Commission, Yojana Bhavan, Parliament Street, New Delhi-1.

Rasul, S. H., B.Sc. (Hons.), M.Sc., Ph.D.Tech., F.P.S., F.G.S., Reader, Head of the Geology Department, Aligarh Muslim University, Aligarh.

*†Rohatgi, H. L., M.Sc., Ph.D., 16/19-G Civil Lines, Kanpur.

*†Roy, Arabinda, M.Sc., Ph.D., Professor of Physiology and Biochemistry, U. P. College of Veterinary Science, Mathura.

*†Sadhu, D. P., M.Sc., Ph.D., Principal, Post-Graduate College of Animal Sciences, I.V.R.I., Izatnagar (U. P.).

Sahai, Rajendra, M.Sc., Asstt. Professor of Botany, University of Gorakhpur, Gorakhpur.

*†Sahni, (Mrs.) Savitri, M.Sc., Director, Birbal Sahni Institute of Palaeobotany, University Road, Lucknow.

†Saksena, B. B. L., M.A., M.Sc., L.T., Assistant Professor of Botany K.N. Govt. Degree College, Gyanpur (Varanasi).

†Saksena, J. N., M.Sc., Assistant Professor in Zoology, Mahakoshal Mahavidyalaya, Jabalpur.

†Saksena, R. D., M.Sc., Ph.D., F.Z.S.I., Professor of Zoology, Balwant Rajput College, Agra.

*†Saksena, R. K., D.Sc., F.N.I., 1 B-Beli Road, Allahabad-2.

*†Saksena, S. B., M.Sc., Ph.D., F.B.S., Reader in Botany, University of Saugar, Sagar.

Sant, H. R., M.Sc., Ph.D., Lecturer, Botany Department, Banaras Hindu University, Varanasi-5.

Sarkar, D. C., Ph.D., Reader and Acting Head of the Physics Department, Muslim University, Aligarh.

Sarma, K. P., M.A., Research Scholar, Department of Mathematics, Osmania University, Hyderabad (A. P.).

*Satyanarayana, Y., B.Sc., Ph.D., Ecologist, Central Arid Zone Research Institute, Jodhpur.

*†Saxena, B. B. L., M.Sc., D.Phil., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

†Saxena, D. B., M.Sc., D.Phil., F.A.Z., M.Z.S., P. G. Department of Zooloogy, J. and K. University, Naseem Bagh, Srinagar.

Saxena, R. K., M.Sc., Lecturer in Mathematics, Govindram Seksaria Technological Institute, Opp. Nehru Park, Indore.

Saxena, Ram Kishore, M.Sc., Ph.D., Lecturer in Mathematics, Faculty of Science, Jodhpur University, Jodhpur.

Saxena, S. C., M.Sc., Ph.D., D.I.C., F.R.E.S., Reader in Zoology, University of Rajasthan, Jaipur.

*†Sen, Bisheswar, B.Sc., Director, Vivekananda Laboratory, Almora.

Sen, D. N., D.Sc., Department of Botany, University of Jodhpur, Jodhpur.

Shanker, Hari, M.Sc., D.Phil., Assistant Professor of Agricultural Chemistry, Govt. Agricultural College, Kanpur.

Sharma, A. P., M.Sc., Lecturer in Physics, D.S. College, Aligarh.

Sharma, B. B., B.Sc.(Hons.), M.Sc , Ph.D., F.B.S., Department of Botany, University of Lucknow, Lucknow.

Sharma, B. M., M.Sc., Lecturer in Biology, Government College, Chittorgarh.

*†Sharma, D., M.Sc., D.Phil., Professor and Head of the Department of Physics, University of Gorakhpur, Gorakhpur.

†Sharma, G. P., M.Sc., Ph.D., F.N.I., F.A.Z., F.I.A.Z., F.Z.S., F.Z.S.I., F.R.M.S., Professor and Head of the Zoology Department, Panjab University, Chandigarh-3.

Sharma, K. C., Ph.D., Lecturer in Mathematics, University of Rajasthan, Jaipur.

Sharma, M. N., M.Sc., Ph.D., F.I.P.S., Grad. I.T.E., Lecturer in Physics, Lucknow University, Lucknow.

Shivahare, G. C., M.Sc., Ph.D., Reader in Chemistry, University of Jodhpur, Jodhpur.

Shiveshwarkar, S. W., B.Sc., M.A., I.C.S., c/o Ministry of Food and Agriculture (Department of Agriculture), Krishi Bhavan, New Delhi.

Shrivastava, R. K., M.Sc., D.Sc , Asstt. Professor of Zoology, Nagpur University, L.I.T. Buildings, Nagpur.

Shukla, Bhola Nath, M.Sc., Lecturer in Science, Govt. Higher Secondary School, Janjgir (Distt. Bilaspur) M. P.

Shukla, G. S., M.Sc., Ph.D., Assistant Professor of Zoology, University of Gorakhpur, Gorakhpur.

Siddiqui, Md. Mahfooz Ali, M.A., B.Sc., Ph.D., Lecturer in Mathematics, Osmania University, Hyderabad-7 (A. P.).

Sidhu, G. S., B.Sc.(Hons.), M.Sc., Ph.D., Deputy Director-in-Charge, Regional Research Laboratory, Hyderabad-9.

*†Singh, Amar, M.Sc., D.Phil., Assistant Professor of Botany, University of Allahabad, Allahabad.

†Singh, Babu, M.Sc., Ph.D., D.I.C., Professor of Botany, Government Agricultural College, Kanpur.

*Singh, Balwant, D.Sc., F.R.I.C., P.E.S.I. (Retd.), Head of the Chemistry Department, Panjabi University, Patiala.

*Singh, B. N., M.Sc., Ph.D., D.Sc., Director (Microbiology), Central Drug Research Institute, Lucknow.

Singh, C. M., M.Sc., Ph.D., Professor of Pathology and Bacteriology, U.P. College of Veterinary Science and Animal Husbandry, Mathura.

Singh, D. V., M.Sc., Senior Research Assistant, Section of Plant Pathologist to Government, U. P., Kanpur.

†Singh, Eric John, M.Sc., D.Phil., Department of Pharmacology, Baylor University, Medical Center, Houston, Texas (U.S.A.).

Singh, J. S., M.Sc., Research Scholar, Department of Botany, Banaras Hindu University, Varanasi-5.

†Singh, P. N., M.Sc., D.Phil., Asstt. Soil Chemist, Soil Testing Laboratory, 24 Paota, Jodhpur.

*Singh, R. N., M.Sc., D.Phil., Principal, Govt. Arts and Science College, Durg (M. P.).

Singh, R. N., M.Sc., Research Assistant, Botany Division, Indian Agricultural Research Institute, New Delhi-12.

Singh, R. P., M.Sc., Lecturer in Mathematics Statistics), M. V. Mahavidyalaya, Bhopal (M. P.).

Singh, Sant, M.Sc., Ph.D., Reader in Agricultural Chemistry and Head of the Agricultural Chemistry Section, College of Agriculture, Banaras Hindu University, Varanasi-5.

Singh, S. P., M.Sc., c/o Dr. B. D. Pande, 1102 West Oregaon Street, Urbana, Illinois (U. S. A.).

Singh, Uma Shankar, M.Sc. Tech., Dr. Ing., Sectional Engineer, Balpahar Refractories Ltd., P. O. Karuppur (Distt. Salem) Madras State.

†Singh, U. S., M.Sc., Vigyan Ratna, D.Phil., Cotton Physiologist, Govt. Cotton Research Station, Raya (Mathura).

Sinha, A., M.Sc., Ph.D., A.R.I.C., Technologist, P. & D., F.C.I. Ltd., R.K. 2/51-Rorha Bandh, P. O. Saharpura, Sindri (Dt. Dhanbad) Bihar.

Sinha, B. M., M.Sc., Ph.D., Professor of Zoology, Meerut College, Meerut.

Sinha, K.P.D., M.Sc., Ph.D., Professor of Mathematics, Bihar University, L. S. College, Muzaffarpur.

Sinha, N. S., B.Sc. (Agri.), Assoc.I.A.R.I., Physiological Chemist, Crop Physiology Section, T. G. Civil Lines, Lucknow.

Sinha, S., M.Sc., Ph.D., Head of the Department of Botany, Agra College, Agra.

†Sreeramulu, T., M.Sc., Ph.D., D.I.C., Reader in Botany, Andhra University, Waltair (A.P.).

Srivastava, A. S., M.Sc., D.Phil., Ph.D., Entomologist to Government and Officer-in-Charge, Plant Protection Service, U. P., Kanpur.

Srivastava, B. K., M.Sc., D.Phil., Asst. Professor of Zoology, Unversity of Saugar, Sagar.

*†Srivastava, B. N., D.Sc., F.N.I., Professor of General Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 32.

Srivastava, B. N., M.Sc., Lecturer in Chemistry, D. A. V. College, Dehra Dun.

Srivastava, C. M., M.Sc., Lecturer in Zoology, Ranchi College, Ranchi.

*†Srivastava, D. S , M.Sc., Ph.D., F.R.M.S., F.R.E S., Professor and Head of the Department of Zoology, University of Saugar, Sagar.

*Srivastava, G. D., M.Sc., B-Beli Road, Allahabad-2.

*Srivastava, H. D., M.Sc., D.Sc., F.N.I., Director, Indian Veterinary Research Institute, Izatnagar.

Srivastava, H. M., M.Sc., Lecturer in Mathematics, University of Jodhpur, Jodhpur.

Srivastava, H. P., M.Sc., Research Scholar, Department of Botany, Allahabad University, Allahabad.

†Srivastava, K. N., M.Sc., D.Phil., Lecturer in Mathematics, M. A. College of Technology, Bhopal (M. P.).

*†Srivastava, M. D. L., D.Sc., Professor and Head of the Department of Zoology, University of Allahabad, Allahabad.

†Srivastava, O. N., M.Sc., D.Phil., Head of the Department of Zoology, K. N. Govt. College, Gyanpur (Varanasi).

*†Srivastava, P. L., M.A., D.Phil., F.N.I., Vice-Chancellor, Bihar University, Muzaffarpur.

†Srivastava, (Miss) Pramila, M.A., D.Phil., D.Sc., Reader in Mathematics, Banaras Hindu University, Varanasi-5.

Srivastava, P. S., M.Sc., Department of Zoology, S. B. R. College, Bilaspur (M. P.).

Srivastava, Rajendra Prasad, M.Sc., Ph.D., Assistant Professor of Zoology, University of Lucknow, Lucknow.

†Srivastava, R. K., B.V.Sc. & A. H., Department of Diary Science, Louisana State University, Baton Rouge (U.S.A.).

Srivastava, R. P., M.Sc., Head of the Physics Dept., S. B. R. College, Bilaspur (M. P.).

†Srivastava, S. K., B.Sc. (Hons.), M.Sc., Kokaghat, Uprahti, Rewa.

Srivastava, S. P., M.Sc., D.Phil., Assistant Professor of Chemistry, D. S. B. Govt. Degree College, Naini Tal.

*†Srivastava, U. S., M.Sc., M.Ed., D.Phil., Professor of Zoology, University of Bihar, Muzaffarpur.

Sundararajan, P. K., B. A. (Hons.), Lecturer in Mathematics, St. Francis de Sales' College, Seminary Hills, Nagpur.

Sukhani, T. R., M.Sc., Lecturer in Zoology-Entomology, Government Agricultural College, Kanpur.

*Sur, N. K., D.Sc., F.N.I., 74 Tagore Town, Allahabad-2.

*†Swarup, H., M.Sc, Ph.D., F.S.Z., Professor and Head, School of Studies in Zoology, Vikram University, Ujjain.

Swarup, K., M.Sc., D.Phil., Department of Zoology, University of Gorakhpur, Gorakhpur.

*Tandon, Amar Nath, M.Sc., D.Phil., Seismologist, Meteorological Office, Lodi Road, New Delhi-3,

Tandon, M. P., M.Sc., D.Phil., Assistant Professor of Botany, University of Allahabad, Allahabad.

*†Tandon, R. N., M.Sc., Ph.D., D.I.C., F.A.Sc., F.N.I., Professor and Head of the Department of Botany, University of Allahabad, Allahabad.

*†Tandon, R. S., M.Sc., D.Phil., F.A.Z., F.H.S., Assistant Professor of Zoology, University of Lucknow, Lucknow.

*†Tandon, S. P., M.Sc., D.Phil., Assistant Professor of Chemistry, University of Allahabad, Allahabad.

Teeka Rao, G., M.A., Lecturer in Mathematics, Department of Chemical Technology, Osmania University, Hyderabad Dn.

*†Tewari, H. B., M.Sc., D.Phil., Assistant Professor of Zoology, University of Lucknow, Lucknow.

†Tewari, Col. S. G., M.Sc., 4, Balrampur House, Allahabad-2.

*Thind, K. S., M.Sc., Ph.D., Reader in Botany, Panjab University, Chandigarh-3.

Tiagi, Yagya Datta, M.Sc., Ph.D., Assistant Professor of Botany, University of Saugar, Sagar.

†Tiwari, I. P., M.Sc., Assistant Professor of Zoology, Government College of Science, Raipur.

*†Tiwari, R. D., M.Sc., D.Phil., Asstt. Professor of Chemistry, University of Allahabad, Allahabad.

Tripathi, L. M., M.A., Research Scholar in Mathematics, Allahabad University, Allahabad.

Tripathi, O. N., M.Sc., LL.B., Ph.D., Head of the Department of Chemistry, Govt. Degree College, Ambikapur, Distt. Sarguja (M. P.).

Tripathi, Y. R., D.Sc., Deputy Director, Fisheries, Department of Animal Husbandry and Fisheries, Badshah Bagh, Lucknow.

Upadhya, V. N., M.Sc., F.P.S., Professor of Physics, S. B. Garda College, Navsari.

Varkey, T. J., M.Sc., Head of the Chemistry Department, Karnataka Regional Engineering College, Surathkal P. O. (Mysore State).

*†Varma, D. N., M.Sc., D.Phil., F.A.Z., New Darbhanga Colony, 29 C. Y. Chintamani Road, Allahabad-2.

*Venkataraman, G. S., M.Sc., Ph.D., F.N.G.S., Microbiologist (Algae), Division of Microbiology, Indian Agricultural Research Institute, New Delhi-12.

Verma, C. B. L., M.A., Professor of Mathematics, Maharaja's College, Chattarpur (M. P.).

Verma, D. M., M.Sc., Technical Assistant, Central Circle, Botanical Survey of India, 10 Chatham Lines, Allahabad-2.

*Verma, G. S., M.Sc., Ph.D., F.L.S., F.R.Hort.S., F.B.S., Reader in Botany, University of Lucknow, Lucknow.

Verma, S. C., M.Sc.(Hons.), Lecturer in Botany, Panjab University, Chandigarh.

Verma, V. K., M.Sc., Ph.D., Department of Mathematics, M. A. College of Technology, Bhopal.

†Vyas, K. D., B.Sc., M.B.B.S., Assistant Professor of Bacteriology, Department of Home Science, University of Allahabad, Allahabad.

Vyas, L. N., M.Sc., Ph.D., Head, Department of Botany, M. B. College, Udaipur (Rajasthan).

*†Wadia, D. N., M.A., D.Sc., F.G.S., F.A.S., F.N.I., F.R.S., Geological Adviser the Govt. of India, Department of Atomic Energy, South Block, Central Secretariat, New Delhi.

*†West, W. D., M.A., Sc.D., F.A.S., F.N.I., Professor and Head of the Department of Applied Geology, University of Saugar, Saugar.

†Weyl, Nathaniel, B.Sc., F.I.A.L., Writer, 4201 S Ocean Blyd., Delroy Beach, Fla. (U. S. A.).

Wilson, K. I., M.Sc., 101 P. G. Hostel, Old Wing, I A.R.I., New Delhi-12.

†Yadav, J. S. P., M.Sc.Ag., Ph.D., A.I.A.R.I., Dip.For., F.C.S., Soil Chemist, Forest Research Institute and Colleges, P. O. New Forest Dehra Dun.

Yadav, R. S., M.Sc., Lecturer in Physics, Muslim University, Aligarh.

*†Zaheer, S. H., M.A., Dr. Phil.Nat., Director General, Council of Scientific and Industrial Research, Rafi Marg, New Delhi-1.

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CONTENTS

		Page
Thirty-third Annual Meeting	*Arun K. Dey*	1
Programme		3
Secretaries' Report	*Dr. R. K. Saksena*	5
Presidential Address	*Prof. P. Maheshwari*	11
Symposium on the Chemistry of National Products : (Abstracts of Papers)		25
Symposium on Land Fertility, Improvement and Alkali Soil Reclamation By Blue Green Algae		33
Appendix I. Council for 1964		35
Appendix II. List of Journals on Exchange List		36
Appendix III. List of Members and Fellows		39

Published by Dr. R. K. Saksena, for the National Academy of Sciences, India, Allahabad and Printed at The Mission Press, Allahabad

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